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STUDY OF ELECTROLYTIC REDUCTION OF CARBON DIOXIDE

TECHNICAL DOCUMENTARY REPORT No. MRL-TDR-62-16

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LIFE SUPPORT SYSTEMS LABORATORY
6570th AEROSPACE MEDICAL RESEARCH LABORATORIES
AEROSPACE MEDICAL DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 6373, Task No. 637302

(Prepared under Contract No. AF 33(616)-7349 by Horace W. Chandler and Willem Oser of the Isomet Corporation, Palisades Park, New Jersey)

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FOREWORD

Work reported here was performed at Isomet Corporation, Palisades Park, New Jersey, from 1 October 1960 to 30 September 1961, by Dr. Horace W. Chandler and Dr. Willem Oser, under Contract No. AF 33(616)-7349 with the Life Support Systems Laboratory, 6570th Aerospace Medical Research Laboratories. The work was in support of Project No. 6373, "Equipment for Life Support in Aerospace," Task No. 637302, "Respiratory Support Equipment." The work performed by Professor T.I. Taylor of Columbia University, who served as a consultant to this project, is gratefully acknowledged. Richard E. Bennett, Respiratory Equipment Section, Sustenance Branch, Life Support Systems Laboratory, served as contract monitor.

ABSTRACT

Electrolytic methods for regeneration of oxygen from carbon dioxide were studied to design a closed-cycle life support system. Two different electrolyte systems were studied: molten alkali carbonates and solid oxides. Mixtures of lithium and potassium carbonates were suitable and could be operated in two different fashions. If operated below the decomposition voltage of the alkali carbonates, the decomposition of the carbon dioxide was direct while operation above the decomposition potential involved the intermediate formation of alkali metals and subsequent reduction of the carbon dioxide with the alkali metal. Using solid mixed oxides of thorium with either yttrium or lanthanum as the electrolyte was feasible because of migration of oxygen ions by means of vacancies existing in the anionic lattice. Cells operate in the temperature range from 400° to 900°C and gas chromatographic analyses have demonstrated the production of oxygen from carbon dioxide.

PUBLICATION REVIEW

This publication has been reviewed and approved.

Wayne H. McCandless

WAYNE H. McCANDLESS
Chief, Life Support Systems Laboratory

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INTRODUCTION

If man is to exist in a closed ecological system for an extended period of time, it is necessary to provide him with a livable atmosphere. The basic problems of atmosphere control comprise the supply of oxygen and the removal of toxic and combustible gases.

Assuming a metabolic requirement of approximately two pounds of oxygen per man-day and a respiratory coefficient of 0.85, carbon dioxide containing 1.7 pounds of oxygen will be expired per man-day. For a closed system, this oxygen must be recovered.

Isomet Corporation, under the terms of the present contract, has been investigating the direct reduction of carbon dioxide by electrolytic methods. In general, this work has utilized two electrolytes, molten carbonate salts and solid oxides. The work on the solid oxide systems is not as advanced as the work on the molten carbonate electrolytes but has indicated the technical feasibility of these systems. The ultimate usefulness of the solid electrolyte systems appears to be greater than that of the molten carbonates because of their freedom from gravitational effect and corrosion. It would appear, therefore, that further work on the solid oxide electrolyte systems is justified on the basis of its elegance and ultimate utility.

The initial work under this contract was concerned with the use of molten carbonate electrolytes. During the course of this work, however, and as a result of theoretical considerations relating to the electrical conductivity of certain solid oxide systems, a method for electrolytically decomposing carbon dioxide using a solid oxide electrolyte was conceived. The work on the molten carbonate systems was continued and at the same time work on the solid oxide electrolyte system was started. As mentioned previously, the feasibility of the solid oxide electrolyte system has been demonstrated unequivocally and further development is required to build an engineering prototype.

METHODS AND MATERIALS

MOLTEN CARBONATE ELECTROLYTES

THEORETICAL

The general principle of operation of a molten carbonate electrolysis system for reduction of CO_2 involves the decomposition of the carbon dioxide at the cathode in an electrolytic cell containing a mixture of fused carbonates. The complete system results in the conversion of carbon dioxide to carbon and oxygen only.

The fused salt electrolysis system can be operated in two ways to give two different cathode reactions depending upon the voltage imposed on the cell.

(a) Anode (+): $2CO_3^{=} \rightleftarrows 2CO_2 + O_2 + 4e^-$

Cathode (-): $4CO_2 + 4e \rightleftarrows 2CO + 2CO_3^{=}$

$2CO \rightleftarrows CO_2 + C$

$CO_2 \rightleftarrows O_2 + C$

(b) Anode (+): $2CO_3^{=} \rightleftarrows 2CO_2 + O_2 + 4e^-$

Cathode (-): $4Na^+ + 4e^- \rightleftarrows 4Na$

$4Na + 4CO_2 \rightleftarrows 2Na_2CO_3 + 2CO$

$2CO \rightleftarrows CO_2 + C$

$CO_2 \rightleftarrows O_2 + C$

The direct reduction of carbon dioxide at the cathode according to reaction (a) occurring at low voltages, or the liberation of alkali elements such as Na or Li followed by reaction with carbon dioxide according to reaction (b) occurring at higher voltages above the decomposition potential of the fused carbonate lead to the same overall cell reaction:

$$CO_2 \rightleftarrows O_2 + C$$

This assumes complete decomposition of CO within the cell. However, the extent of decomposition of CO in either (a) or

(b) will depend on the temperature of operation, presence of catalysts, residence time, mixing, etc. Thus the cell may be designed and operated under conditions where carbon forms predominantly in the cell or under conditions where CO is formed and decomposed to carbon external to the cell. In either case, the carbon dioxide formed as a result of this decomposition is recycled to the cathode along with carbon dioxide from the vehicle cabin. The oxygen and carbon dioxide produced at the anode are separated and the carbon dioxide returned to the cathode compartment for reduction.

The formation of carbon within the cell requires its removal by filtration or centrifugation. This does not complicate the cell design excessively beyond what would normally be required since, under zero gravity conditions, pumping and centrifugation will also be needed for separation of the gas and liquid phases.

At relatively high temperatures (700°C and above), the formation of carbon monoxide within the cell can be promoted. This mode of operation requires extra equipment for the catalytic conversion of carbon monoxide to carbon but does not require filtration for removal of the carbon.

Another important factor affecting the cell design is the relative extent of cathode reactions (a) and (b). From the nature of these two electrode reactions, it can be seen that a cell for direct reduction of carbon dioxide at the electrode may have different requirements than a cell for liberation of sodium followed by reaction with carbon dioxide. For example, the problem of contacting the carbon dioxide with the electrode over a large catalytically active surface limits the design of the electrode. If sodium is liberated first, carbon dioxide may be contacted with it on the electrode, within the fused salt melt, on the surface of the melt, in the vapor phase, or even in a separate vessel.

EXPERIMENTAL

Current-Voltage Curves:

Operation of cells under a variety of conditions determined some of the factors that must be considered in practical designs. The experiments performed place special

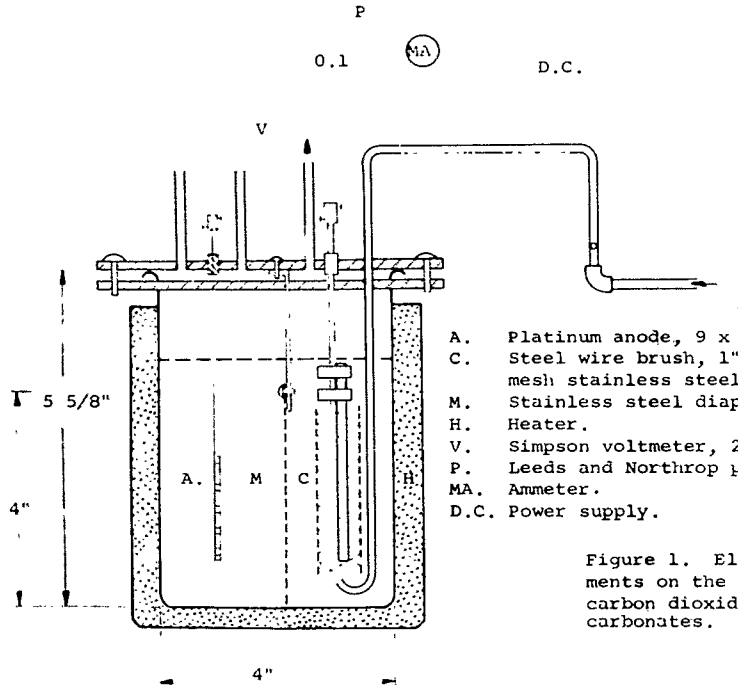
emphasis on current-voltage curves as a function of temperature. From these curves, it is possible to obtain information about the electrode reactions and make some conclusions about the design of the cells for different modes of operation. The cathode used for the experiments reported was suitable for reactions (a) or for reactions (b) as discussed in the previous section.

Apparatus and Procedure:

Figure 1 is a schematic diagram of the electrolyte cell. A stainless steel vessel 4" diameter inside by 5 5/8" high was fitted with a cover which contained openings for electrode leads and for gas inlet and exit tubes. A stainless steel partition and a stainless steel screen (200 mesh) divided the cell into two compartments. The anode was of perforated platinum sheet (9 x 5 cms) and the cathode was a steel wire brush 1" O.D. by 3" long and covered by a 30 mesh stainless steel screen. Its external superficial area was about 60 cm^2. As the carbon dioxide passed through the cathode, it followed a spiral path upward, contacting the small wires of the brush as well as the screen. This provided reasonably large surface area for direct reduction of carbon dioxide. It also provided for partial contact of gaseous carbon dioxide with alkali metal if it should deposit on the stainless steel screen surrounding the wire brush.

The cell was filled with an equal mole mixture of Li_2CO_3, Na_2CO_3, and K_2CO_3 to a point above the wire mesh partition. Current was supplied from a small D.C. power supply through an ammeter to the electrodes. A potentiometer was used to measure the voltage drop across a 0.1 ohm resistor as a more precise determination of the current flowing through the cell. Voltages across the cell were measured with a Simpson meter (20,000 ohms/volt). The temperature of the furnace was controlled with a variable transformer and temperatures were measured with a chromel-alumel thermocouple. A rotameter type flow meter was used to measure the flow of tank carbon dioxide or of argon into the cell.

After the temperature of the cell had been adjusted to the desired value, the current flowing through the cell was measured as a function of voltage across the electrode



A. Platinum anode, 9 x 5 cm.
C. Steel wire brush, 1" O.D. x 3" long with 30 mesh stainless steel screen.
M. Stainless steel diaphram, 200 mesh.
H. Heater.
V. Simpson voltmeter, 20,000 /volt.
P. Leeds and Northrop potentiometer.
MA. Ammeter.
D.C. Power supply.

Figure 1. Electrolysis cell for experiments on the regeneration of oxygen from carbon dioxide by electrolysis in fused carbonates.

terminals. A number of current-voltage curves were obtained with carbon dioxide flowing through the cathode. Argon was then passed through the cathode in the same way and another set of curves was obtained. In each case, readings were taken, first as the voltage was increased, and then as the voltage was decreased. Open cell voltages were obtained by disconnecting one of the leads to the electrodes so that only the voltmeter (20,000 ohms/volt) was in the circuit. At other times, the voltage was read as a function of time with a 10 ohm resistor across the electrodes.

Reaction of Alkali Metals with Fused Carbonates:

The results of the experiments on current-voltage curves during the electrolysis of fused carbonates showed that the cell could be operated in two ways. In one method of operation, there is direct reduction of carbon dioxide at the cathode. In the other method, carbon dioxide is reduced by the alkali metal liberated at the cathode according to the reactions:

Anode (+): $2CO_3^{=} \rightleftarrows 2CO_2 + O_2 + 4e$

Cathode (-): $4Na^{+} + 4e \rightleftarrows 4Na$

$4Na + 4CO_2 \rightleftarrows 2Na_2CO_3 + 2CO$

$2CO \rightleftarrows CO_2 + C$

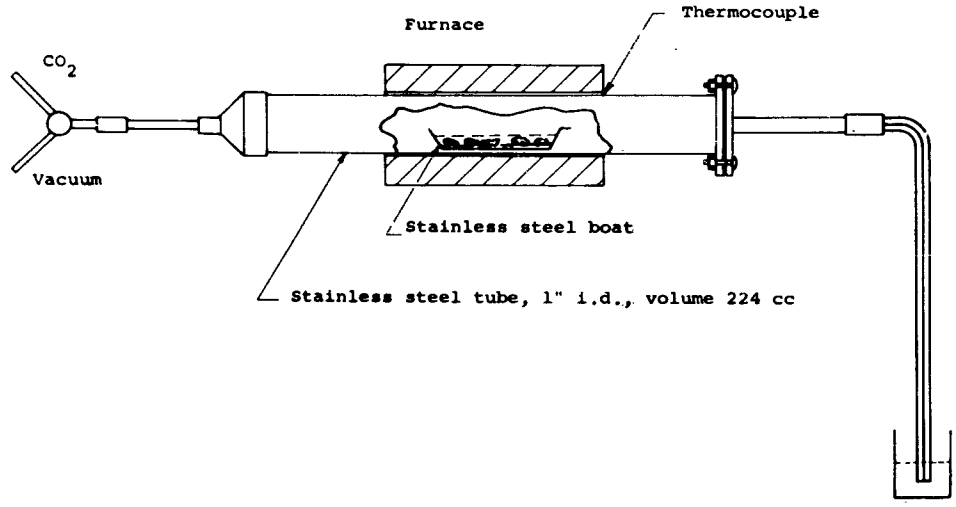
$CO_2 \rightleftarrows C + O_2$

The optimum cell design and method of operation is different for the two ways of operating the cell. If carbon dioxide is to be reacted with the liberated alkali, an efficient means of contacting is needed. It is also of importance to know the conditions under which rapid reaction occurs.

Apparatus and Procedure:

Preliminary experiments carried out in glass equipment showed that the temperature required for the rapid reaction of sodium with carbon dioxide was rather high. The system finally chosen for the experiments was constructed with a stainless steel tube as shown in Figure 2. An O-ring flange on the stainless steel tube allowed the introduction of a stainless steel boat containing the alkali element. The tube was 1" i.d. with a total volume of 224 cc. A three-way stopcock attached

Figure 2. System for experiments on the reaction of carbon dioxide with lithium, sodium, and potassium.



to the 1/4" stainless steel tube on one end allowed either evacuation of introduction of carbon dioxide. The pressure was followed by means of a 3 mm capillary tube with its lower end in a jar of mercury.

The procedure for an experiment was as follows:
With carbon dioxide flowing through the tube at room temperature, a weighed quantity of alkali metal in a stainless steel boat was slid to the center section of the furnace. In each case, a small stainless steel screen was pressed on the alkali metal. This was done to distribute the heat of the reaction and to determine whether the alkali metal wetted the wire when it melted. After closing the tube, the system was evacuated and carbon dioxide was then let in at the desired pressure, usually 35 to 40 cm of mercury. A variable transformer connected to the furnace was set at a voltage to give a final temperature of 500 to 600°C. During the run, the voltage was increased when the rate of temperature rise was too slow.

SOLID OXIDE ELECTROLYTES

Theoretical:

In certain mixed oxide systems, notably the ZrO_2-Y_2O_3, ZrO_2-CaO, ThO_2-Y_2O_3, ThO_2-La_2O_3 systems, solid solutions are formed. These solid solutions form anomalous mixed crystals in which there are vacant places (holes) distributed statistically at random throughout the anion component lattice. These make it possible for O^{--} ions to jump from "hole to hole" and, therefore, to migrate in an electric field. As an example, in a solid solution of the system ZrO_2-Y_2O_3 with the composition 1 mole ZrO_2 + 1 mole $YO_{1.5}$, 25 percent of the anion positions in the statistically random distributions are are unoccupied.

A great number of attempts and proposals have been made prior to this to produce such a solid conductor. As such a solid conductor, a mixture of clay, cerium dioxide in the form of residues from the ignition of monazite, and tungsten trioxide has been suggested by Baur and Preis (Zeitschrift fur Electrochemie, 43,727, 1937). This solid conductor was not, however, satisfactory for practical purposes since in continuous operation the material underwent irreversible changes rather rapidly.

Another disadvantage of this electrolyte was the fact that a sufficiently high conductivity was not reached except at very high temperatures of approximately 1100°C. Such high temperatures are extremely disadvantageous in practical operation, since they require a great expenditure for heat insulation in order to keep the heat losses within reasonable limits. In addition, great difficulties are encountered with respect to the material in building up larger elements.

As was shown by Hund [Z. Anorg. u. Allgem. Chem. 274,105 (1953), Z. Phys. Chem. 201,268 (1952)], the conductivity of this material and of the Nernst mass filament (solid solutions in the system ZrO_2-Y_2O_3) arises from the presence of the aforementioned defect structure.

Based on the principal of electrical conduction by migration of O^{--} ions through the solid, an electrochemical cell can be constructed in which CO_2 is fed in at one electrode and oxygen emerges at the other electrode, the whole system, both electrodes and solid electrolyte being held at a temperature in the range of 400 to 900°C with an electrical potential sufficient to cause the desired rate of decomposition of CO_2 to occur.

EXPERIMENTAL

Solid Electrolyte Preparation:

In order to test the theory described above for its utility in carbon dioxide reduction, solid electrolyte discs of the following mixtures were prepared:

1) ThO_2-La_2O_3
2) ThO_2-Y_2O_3

ThO_2 was used rather than ZrO_2 for several reasons. The conductivity of the ThO_2-rare earth oxide systems is higher than that of the corresponding ZrO_2 systems and, in addition, ThO_2 already has the fluorite structure and is thus more easily analyzed by x-ray diffraction techniques, Hund having already determined the lattice parameters.

The ThO_2-La_2O_3 system consists of 50 mole percent ThO_2 and 50 mole percent La_2O_3. This combination was selected because the fluorite lattice of ThO_2 is capable of forming solid solutions with La_2O_3, up to 52 mole percent La_2O_3.

The finely ground oxide powders (-200 mesh) are thoroughly mixed and then dry-pressed into a disc approximately 1 inch in diameter and 4 mm thick under pressure up to 80 tons/in^2. This disc is then fired in either a platinum wire resistance furnace or an induction heating furnace at temperatures up to 1750°C, the heating and cooling cycle taking up a total of about 18 hours with the furnace being held at the top temperature for about two or three hours.

The discs are fired in an alundum crucible while lying on a platinum plate to eliminate contact between the alundum and the mixed oxide disc. Contact between the disc and the alundum causes the formation of a molten mass rendering the disc unsuitable for use. For firing at temperatures above 1750°C, the platinum plate is unsuitable and a MgO plate has been tried successfully. The alundum crucibles do not possess the high temperature properties necessary for long life at these elevated temperatures so that zirconia crucibles will be used in the future.

The induction heating furnace consisted of an alundum crucible surrounded by a thin layer of powdered alundum insulation. Around this was placed the graphite susceptor cylinder which was, in turn, completely covered by another layer of powdered alundum insulation. The whole system was held inside a quartz cylinder and covered by a heavy sintered alumina cap having a pyrometer sight hole in its center. This hole was covered by insulating brick during firing and was only opened for periodic temperature measurement. The water-cooled copper induction heating coils were wrapped tightly around the quartz cylinder and connected to a 10 KW Lepel T-5 high frequency induction heating unit.

The lifetime of the graphite susceptor was about 3 weeks of continuous operation because of the slow diffusion of oxygen to the susceptor and its consequent burning away. When the susceptor is burned away to a very thin piece a

hole will develop at some point in it. This caused arcing because of the high current flowing in the susceptor and this arcing, in turn, results in the melting of the alundum crucible. It is, therefore, probably a better procedure to establish a regular replacement schedule for the graphite susceptor rather than risk the destruction of the expensive crucible.

After the first firing, the disc is removed from the furnace and ground to a -200 mesh powder again. This powder is pressed under the same conditions as before and refired under the same conditions. This procedure is repeated a total of four times until the proper crystal structure is attained as determined by x-ray diffraction techniques. The final disc is a dense, hard non-porous structure with a reasonable resistance to shock but very little elasticity, being unable to withstand any bending.

In the case of the ThO_2-Y_2O_3 system, a composition containing 72 mole percent ThO_2 and 28 mole percent Y_2O_3 was used. In this instance, this particular combination was chosen because the fluorite lattice of the ThO_2 can form solid solutions with Y_2O_3 up to 30 mole percent Y_2O_3. Again, four firings, with grinding and pressing between firings, were made before the disc attained the desired structure. In all the firing operations, care must be taken to place the disc in a uniformly-heated portion of the furnace to prevent warping of the disc.

Cell Construction:

Various types of cell construction were tried in an attempt to make a gas-tight cell using a solid electrolyte disc. In general, the solid electrolyte disc was placed between two Zircum ceramic cylinders and various gaskets and/or sealing cements were used at the joint in an effort to seal the cell. Electrodes were of silver and were pressed against a layer of finely-ground silver powder in contact with the disc. Power was supplied from a D. C. power supply. Current measurements were made with a milliammeter in series with the cell and the voltage across the cell was measured with a volt-ohmeter.

Measurements:

The variation in conductivity of the ThO_2-Y_2O_3 discs as a function of temperature was measured by applying various voltages to the sintered porous silver electrodes placed on both sides of the solid electrolyte disc and measuring the resultant current at various temperatures with the disc in an air atmosphere. Results of these measurements are shown in Figures 3, 4, and 5.

Experiments were run to observe direct decomposition of CO_2 in cells using the ceramic discs as the electrolyte. Since these cells could not be sealed against air leakage, no quantitative data could be obtained on the rate of decomposition of the CO_2 in these cells. The cell was set up with the solid electrolyte disc and CO_2 was fed to the negative electrode compartment. The positive electrode compartment was flushed with nitrogen or argon and then the inert gas was allowed to flow through the cell at a very slow rate. The gas from the positive electrode compartment was analyzed for oxygen by gas chromatographic techniques.

In addition to the cells constructed using a solid electrolyte disc, a concentric-tube cell was constructed. The solid electrolyte tube was a custom-fabricated zirconia-yttria tube, 1/2 inch in diameter and 11 1/2 inches long. The wall thickness was 2 mm. The central 5 cms of the tube length were filled with silver powder and a platinum lead wire was introduced into the silver. This tube was encased in a pyrex glass jacket and the annular space of the central 5 cms was filled with silver powder. The platinum lead wires were connected to a D. C. power supply. The cell was placed in a furnace to heat the central 5 cms of the tubes. Current and voltage were measured with a milliammeter and volt-ohmeter respectively. The cell temperature was measured with a thermocouple.

The cell was heated to 400°C in the furnace. The inner tube was filled with air at atmospheric pressure and the sealed tube was then connected to a mercury manometer so that any change in pressure in the air compartment could be noted. The outer annular space was filled with CO_2 to a

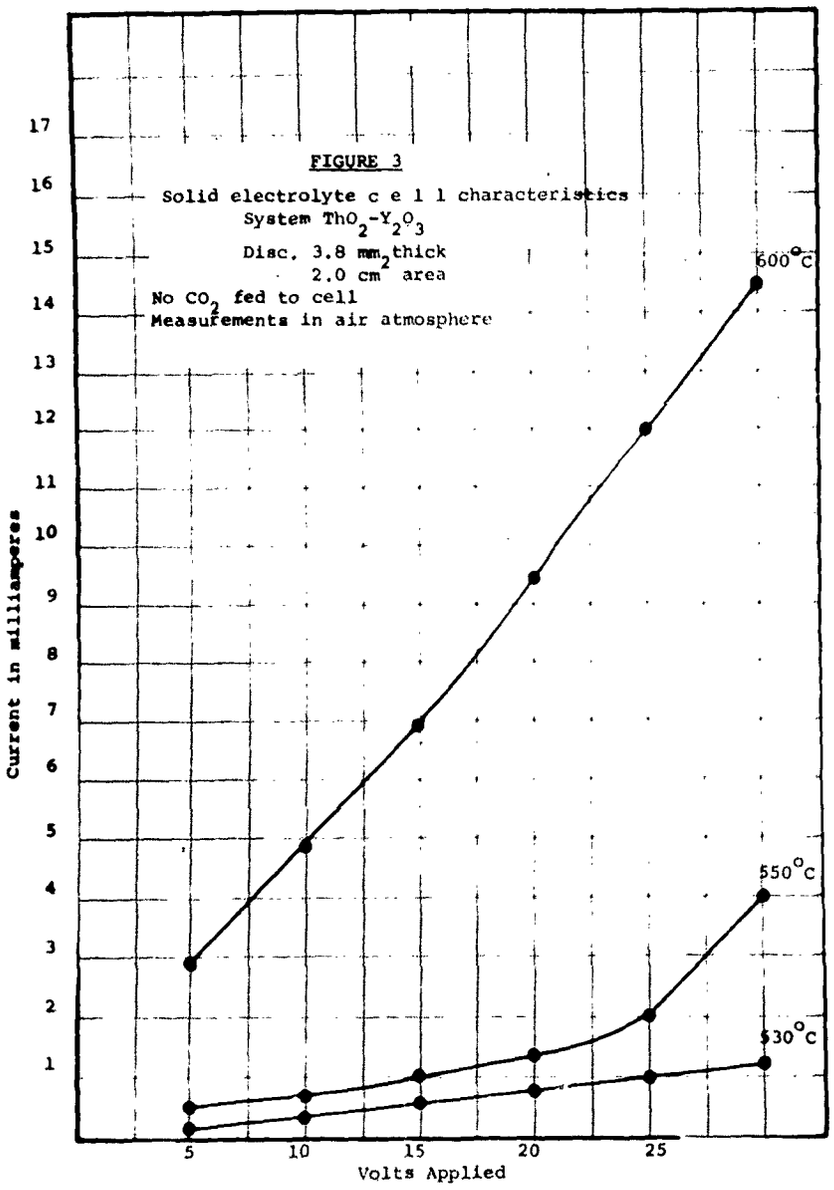


FIGURE 3
Solid electrolyte c e l l characteristics
System ThO_2-Y_2O_3
Disc, 3.8 mm thick
2.0 cm^2 area
No CO_2 fed to cell
Measurements in air atmosphere
600°C
550°C
530°C
Current in milliamperes
Volts Applied
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
5
10
15
20
25

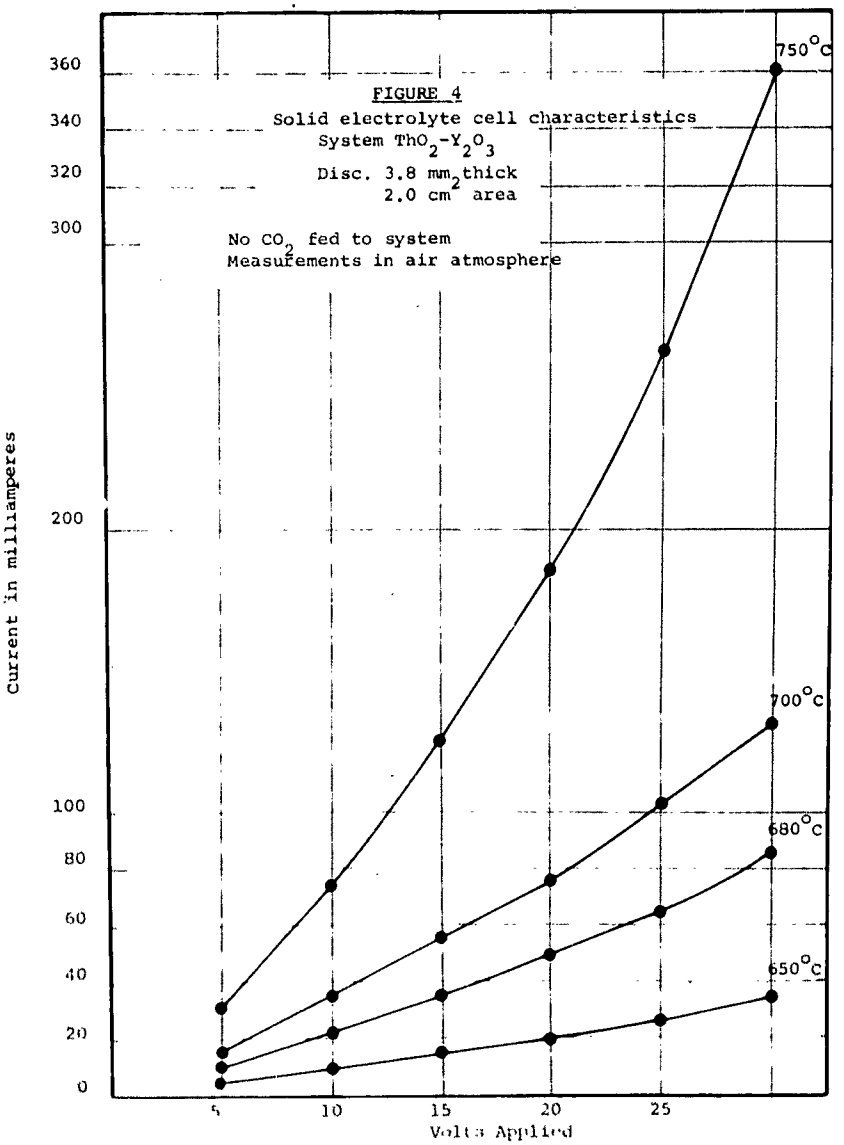


FIGURE 4
Solid electrolyte cell characteristics
System ThO_2-Y_2O_3
Disc. 3.8 mm_2 thick
2.0 cm^2 area
No CO_2 fed to system
Measurements in air atmosphere
750°C
700°C
680°C
650°C
Current in milliamperes
Volts Applied
360
340
320
300
200
100
80
60
40
20
0
5
10
15
20
25

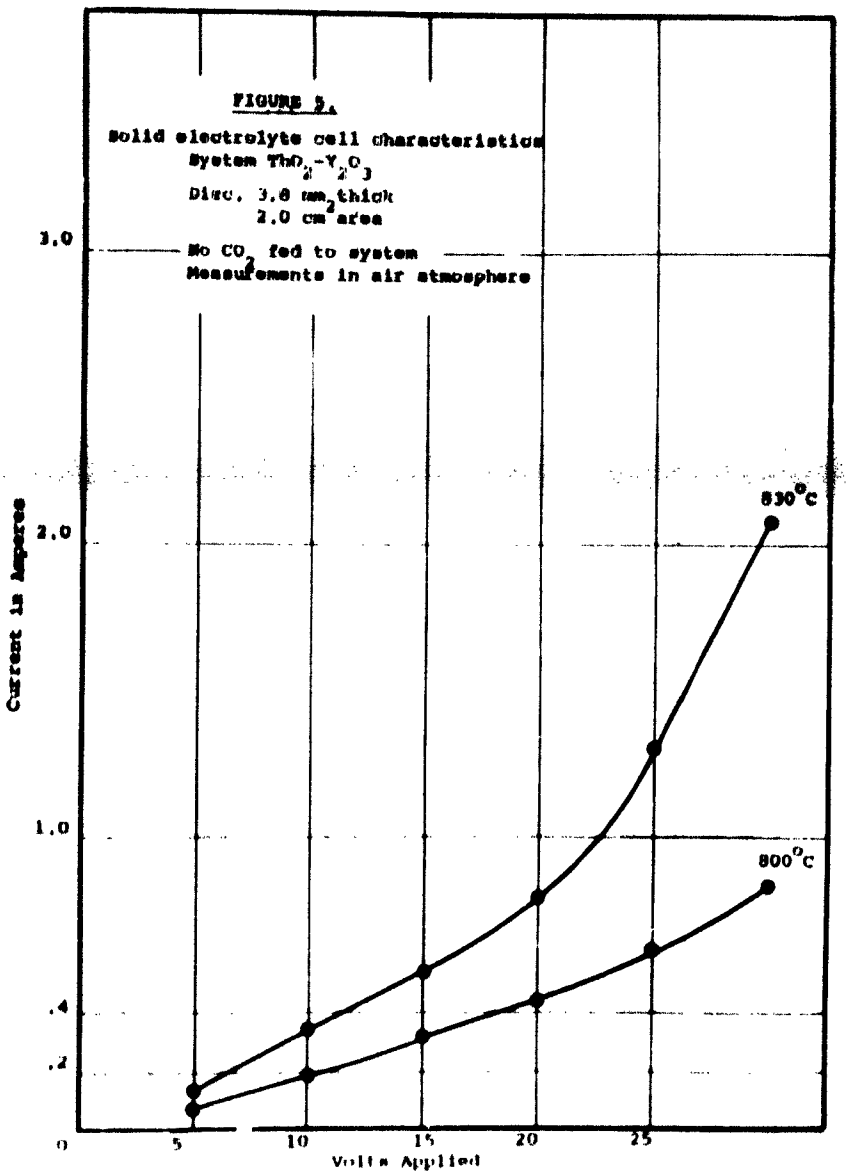


FIGURE 5.
Solid electrolyte cell characteristics
System ThO_2-Y_2O_3
Disc, 3.0 mm thick
2.0 cm^2 area
No CO_2 fed to system
Measurements in air atmosphere
Current in Amperes
3.0
2.0
1.0
.4
.2
0
5
10
15
20
25
Volts Applied
830°C
800°C

pressure of about 5 inches of mercury. The entire apparatus and the solid electrolyte tube were tested and found to be gas tight.

Four volts were applied across the silver electrodes; and under these conditions, a current of 300 milliamps flowed. It was observed that the pressure on the air side of the cell increased as operation continued and that the pressure on the CO_2 side of the cell decreased. Chromatographic analysis of the gas on both sides of the cell was made. Analysis of the gas on the carbon dioxide side showed the presence of carbon monoxide after a period of operation, whereas analysis of the carbon dioxide feed showed no carbon monoxide. Analysis of the gas on the air side showed an oxygen/nitrogen ratio of 0.51 after operation while the oxygen/nitrogen ratio in air was found to be 0.36.

RESULTS AND DISCUSSION

MOLTEN CARBONATE ELECTROLYTES

Typical current-voltage curves obtained during electrolysis of the molten carbonates are shown in Figures 6 through 11. These indicate typical curves at varying and increasing temperatures from 558° to 734°C.

The results with carbon dioxide flowing through the cathode are collected in Figure 12 and those with argon are in Figure 13. For comparison, the current-voltage curve shown in Figure 14 was obtained in a smaller apparatus with a platinum crucible and a platinum electrode as illustrated in the diagram with the curve.

At temperatures as low as 558°C (Figures 6 and 12), there appears to be little direct reduction of carbon dioxide since the current-voltage curve is not greatly different from that obtained with argon. As the temperature is increased to 610°C (Figures 7 and 12), the extent of direct reduction of carbon dioxide increases as shown by the initial part of the curve with carbon dioxide. When the voltage is increased above 1.9 volts, alkali metal is apparently formed since the slope of the current-voltage curve follows the one obtained with argon. Furthermore, the dotted curve obtained with decreasing voltage is that expected for an electrode on which alkali metal had deposited. The fact that the curve at 610°C with decreasing voltage did not follow the one for increasing voltage indicates that either the contact between the carbon dioxide and liberated alkali metal is not good or that the reaction rate is slow.

As the temperature is increased further, the extent of the direct reduction of carbon dioxide increases as shown in Figures 8, 9, and 12. The results at 714°C (Figures 10 and 12) are interesting because they show more clearly the

FIGURE 6. Current-voltage curves with carbon dioxide and with argon at 558°C

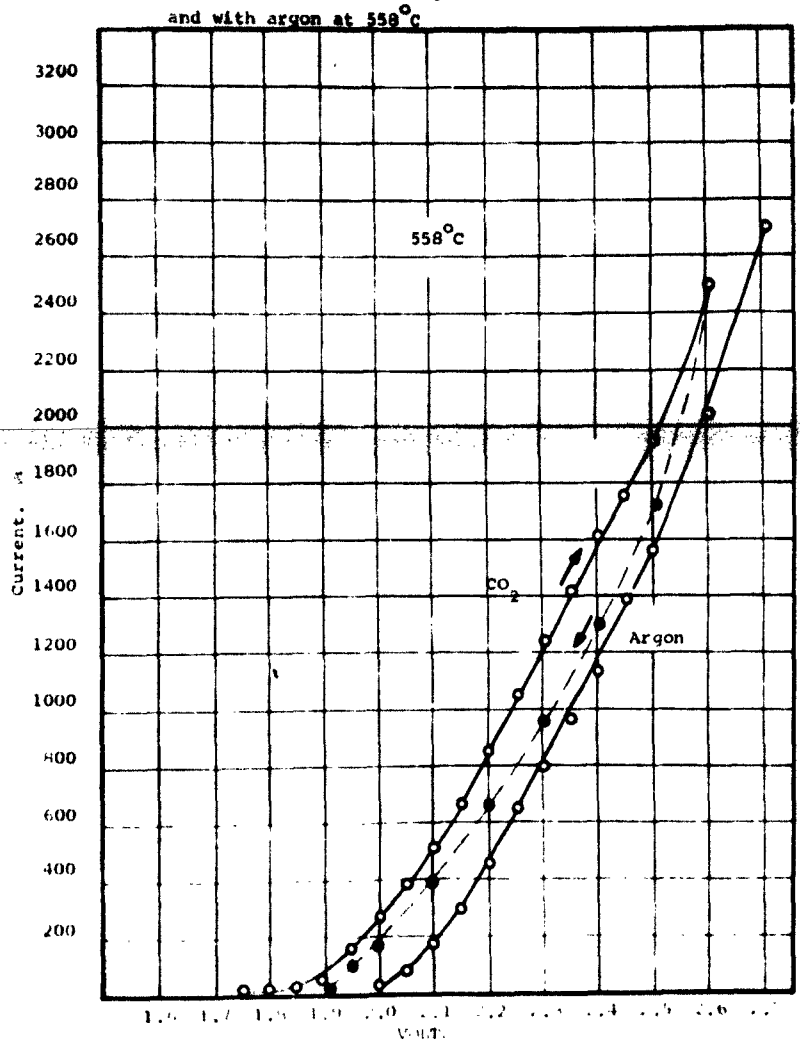


FIGURE 7. Current-voltage curves with carbon dioxide and with argon at 610°C

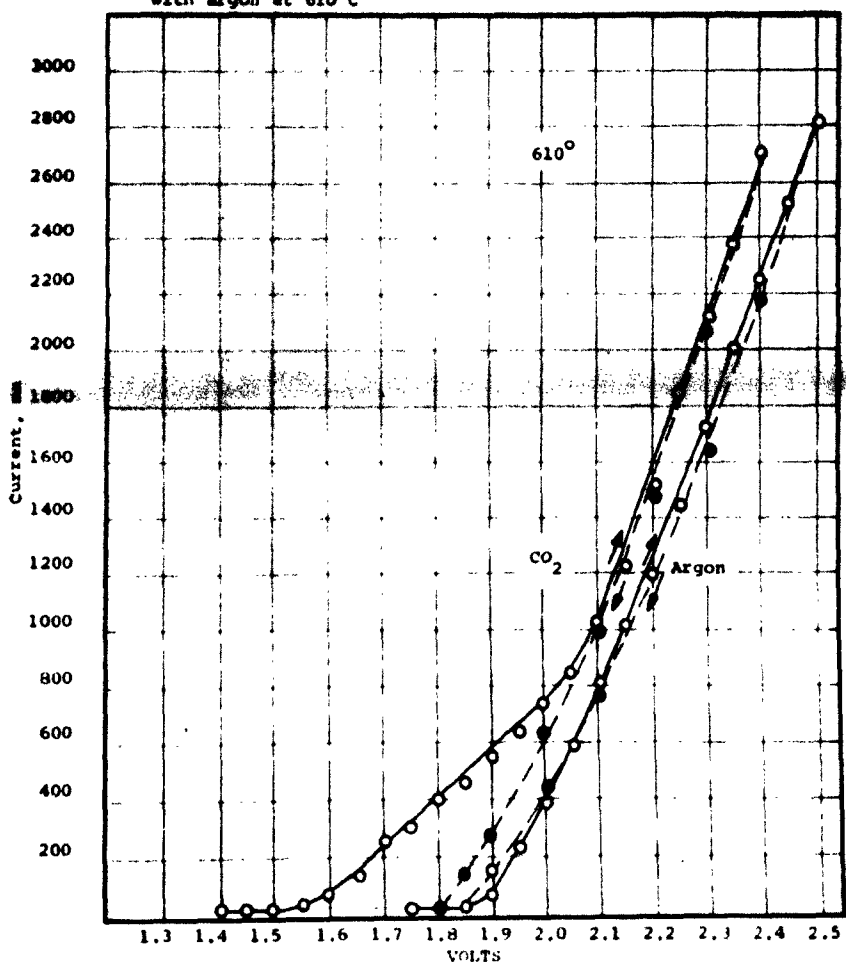


FIGURE 8. Current-voltage curve with carbon dioxide at 636°C

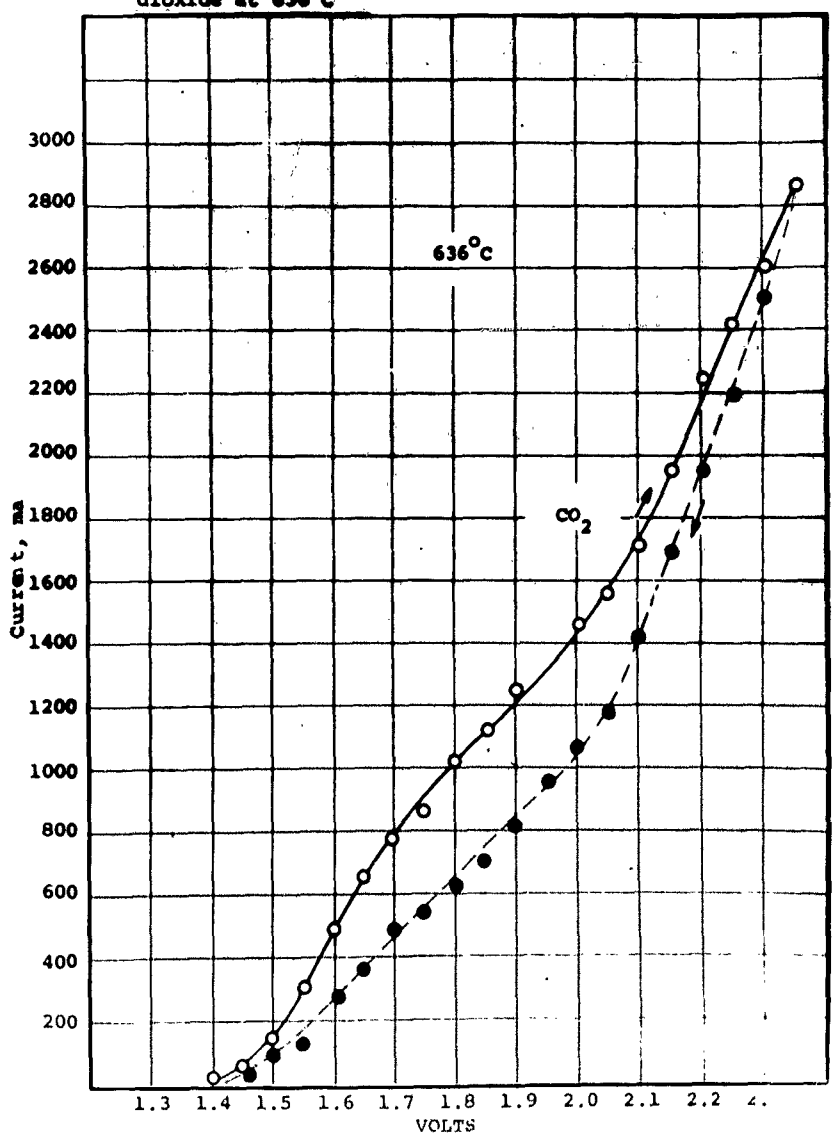


FIGURE 9. Current voltage curves with carbon dioxide and argon at 684°C

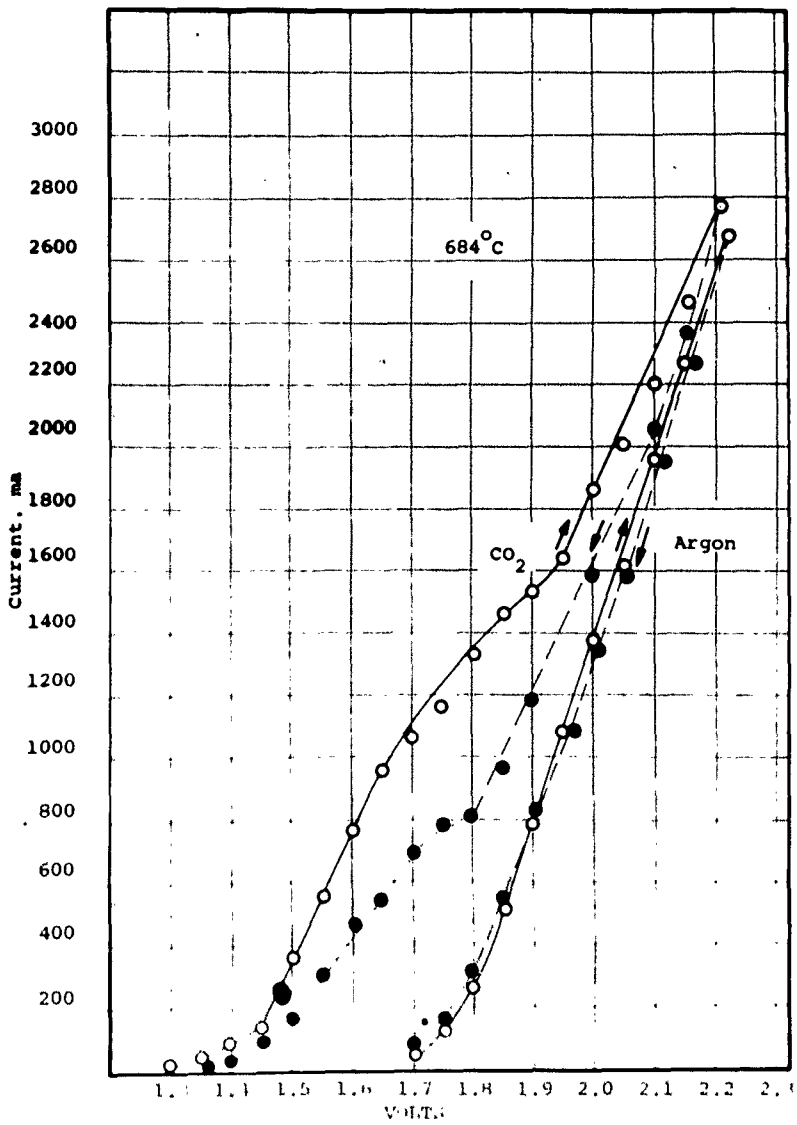


FIGURE 10. Current voltage curves with carbon dioxide at 714°C.

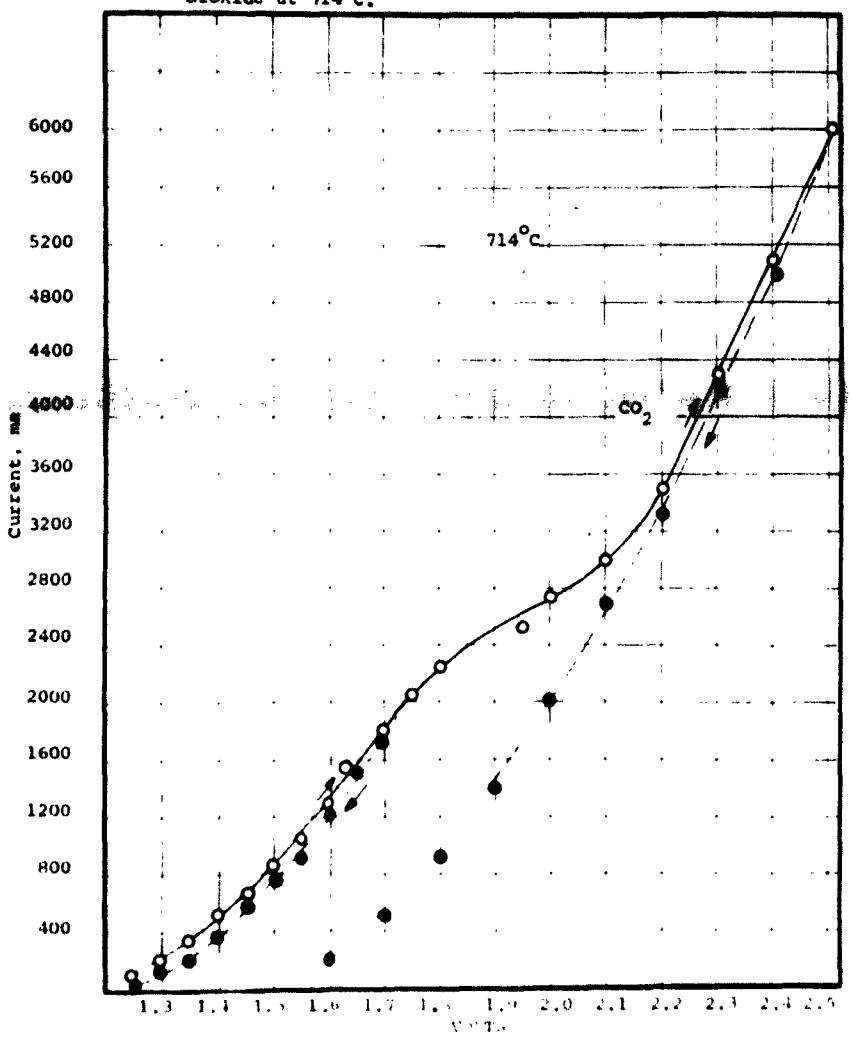


FIGURE 11. Current voltage curves with carbon dioxide and argon at 734°C

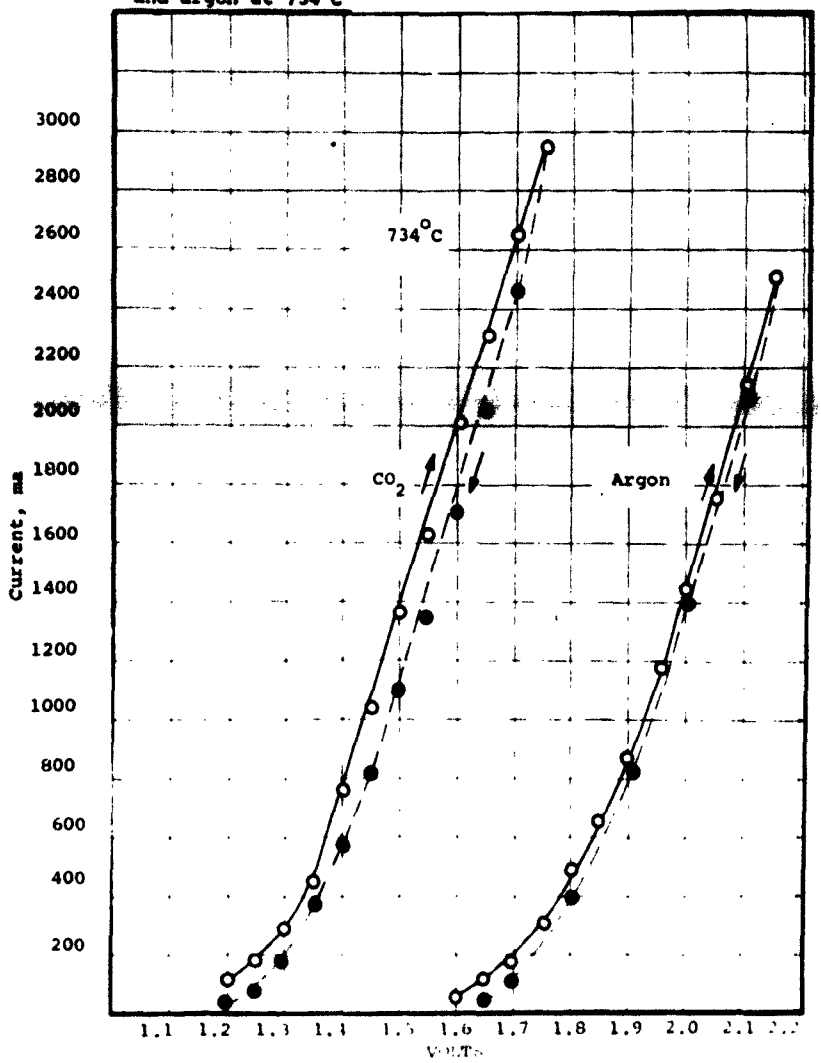


FIGURE 12. Summary of current voltage curves with carbon dioxide flowing through the cathode.

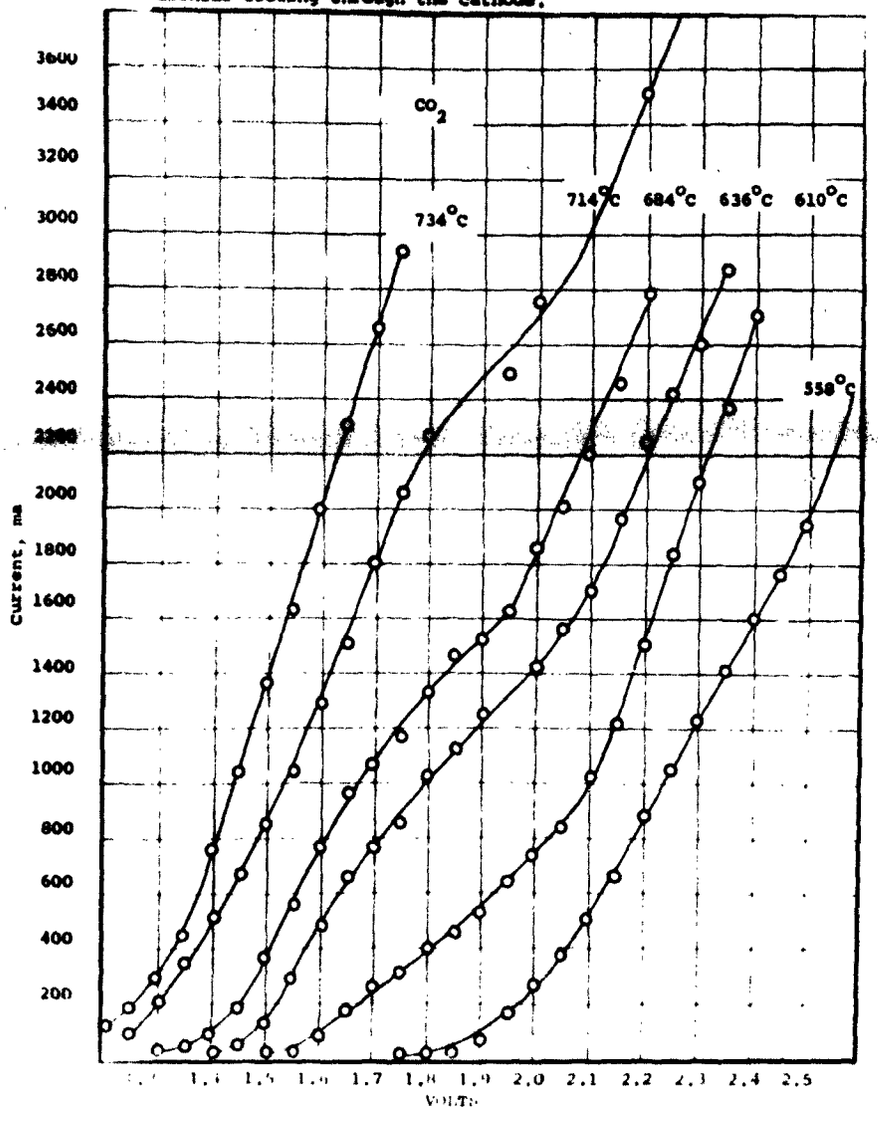
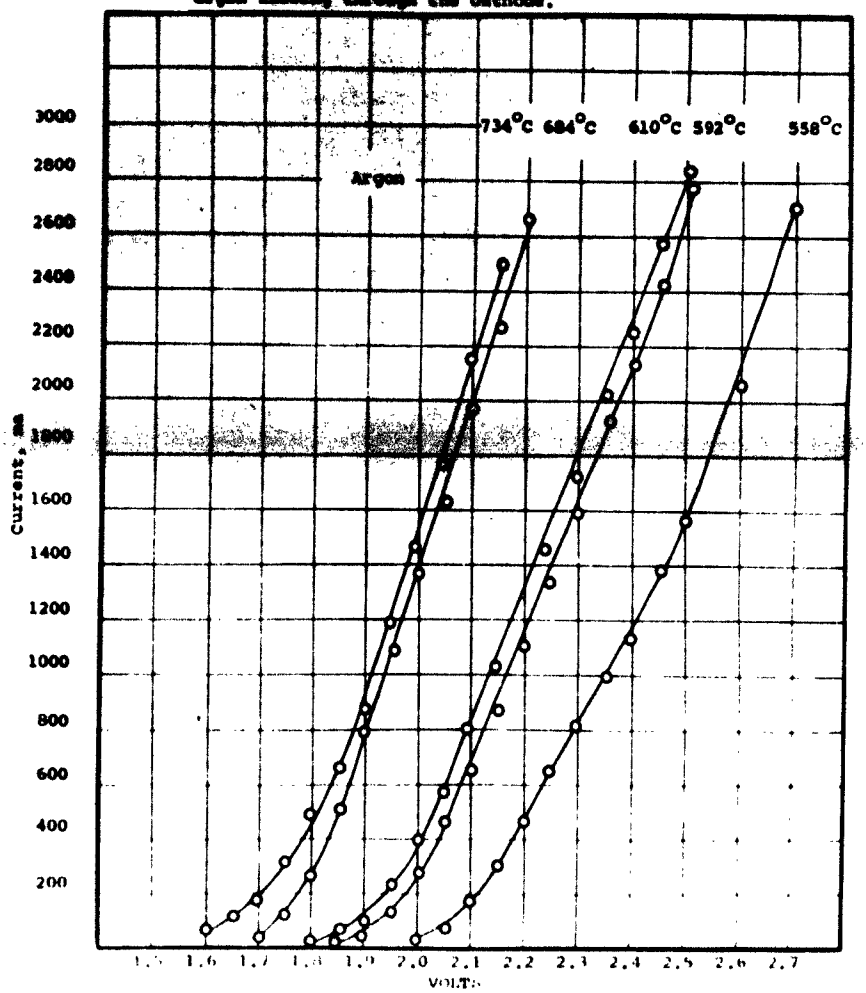


FIGURE 13. Summary of current voltage curves with argon flowing through the cathode.

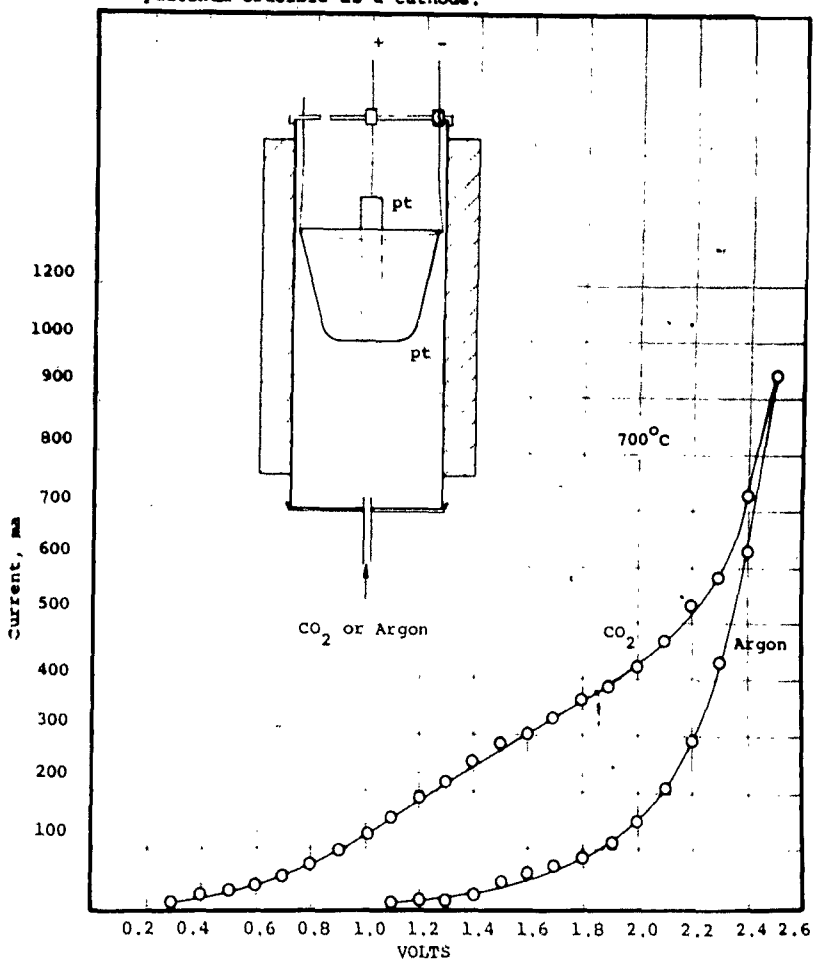


effect of deposition of alkali metal on the cathode. When the maximum voltage was only 1.7 volts, the curve with decreasing voltage was essentially the same as the one for increasing voltage. The current flowing at 1.75 volts was 2200 ma or a current density of 2200 ma/60 cm^2 = 36.5 ma/cm^2, based on the superficial area of the electrode. With increasing voltage and current, the curve changes to that expected for alkali metal deposition. When current has passed through the cell at the higher voltages, alkali metal is apparently deposited on the electrode as indicated by the curve obtained with decreasing voltage.

Only when the temperature is as high as 734°C does one obtain rapid direct reduction of carbon dioxide without liberation of alkali metal. This is shown in Figure 11 where currents as high as 3 amperes pass through the cell without liberation of alkali metal. The curves with increasing and decreasing voltages are about the same. At higher current densities, simultaneous reduction of carbon dioxide and liberation of alkali metal would probably occur.

The effect of the surface area of the cathode on the direct reduction of carbon dioxide is indicated by comparison of the curves in Figure 12 with the curve in Figure 14. The curves with the platinum crucible and platinum electrode show the same qualitative behaviour but the extent of the direct reduction of carbon dioxide is appreciably lower. Since the qualitative behavior of the two cells is similar, it is inferred that the metal of the cathode in the large cell was not directly involved in the electrochemical reactions. In another experiment with the platinum crucible, the platinum anode was replaced by a silver screen electrode. Silver was found plated out on the platinum crucible and the current-voltage curve indicated that this was occurring. Evidently, the oxygen liberated on the silver forms silver oxide which dissolves in the melt and the silver plates out on the platinum crucible which was the cathode.

FIGURE 14. Decomposition curves with a platinum anode and a platinum crucible as a cathode.



Frequent readings of the open circuit voltage were made by disconnecting the lead from the cell to the power supply. If these readings were taken with argon flowing through the cell, the voltage obtained was from 1.7 to 2.0 depending on the temperature. The voltages were essentially the same as the decomposition voltages in Figure 13. When carbon dioxide was passed through the system, the open circuit voltage depended on the voltage at which the cell had been operating just previously to breaking the circuit. If the circuit were opened while the cell was running at the higher voltages (2 to 2.5 volts), the open cell voltage was from the 1.7 to 2.0 volts depending on the temperature. These are the values expected for a cathode on which alkali element is deposited. At temperatures above 700°C or after the cell had operated below 2 volts, the open circuit voltages were from 1.0 to 1.5 volts depending on the temperature. That is, they were about the same as the decomposition voltages shown in Figure 12. Thus, the behaviour of the system with respect to open-circuit voltages is consistent with the current-voltage curves.

Several measurements were made on the changes in the voltage and current as a function of time of discharge on the cell. For example, the results shown in Figure 15 on the following page are for the discharge of the cell after it had operated with carbon dioxide at 610°C. The rate at which the voltage and current decreased varied with the resistance in series with the cell, the time the cell had operated, the temperature, the flow of carbon dioxide, etc. With the volt-meter (20,000 ohms per volt) alone across the terminals of the cell, the decrease in voltage of the cell was slow, from 1.5 to 1.4 volts in 30 minutes for one experiment. This again varied with the manner in which the cell had been operated. These results indicate that the oxygen liberated at the cathode during electrolysis and the carbon were functioning as an electrochemical fuel cell.

The effect of replacing carbon dioxide with argon, or of replacing argon with carbon dioxide, is illustrated in Figure 16. When the voltage was maintained at 1.5 during

FIGURE 15. Change in voltage and current during discharge through a 10Ω resistor after electrolysis with carbon dioxide at 610°C.

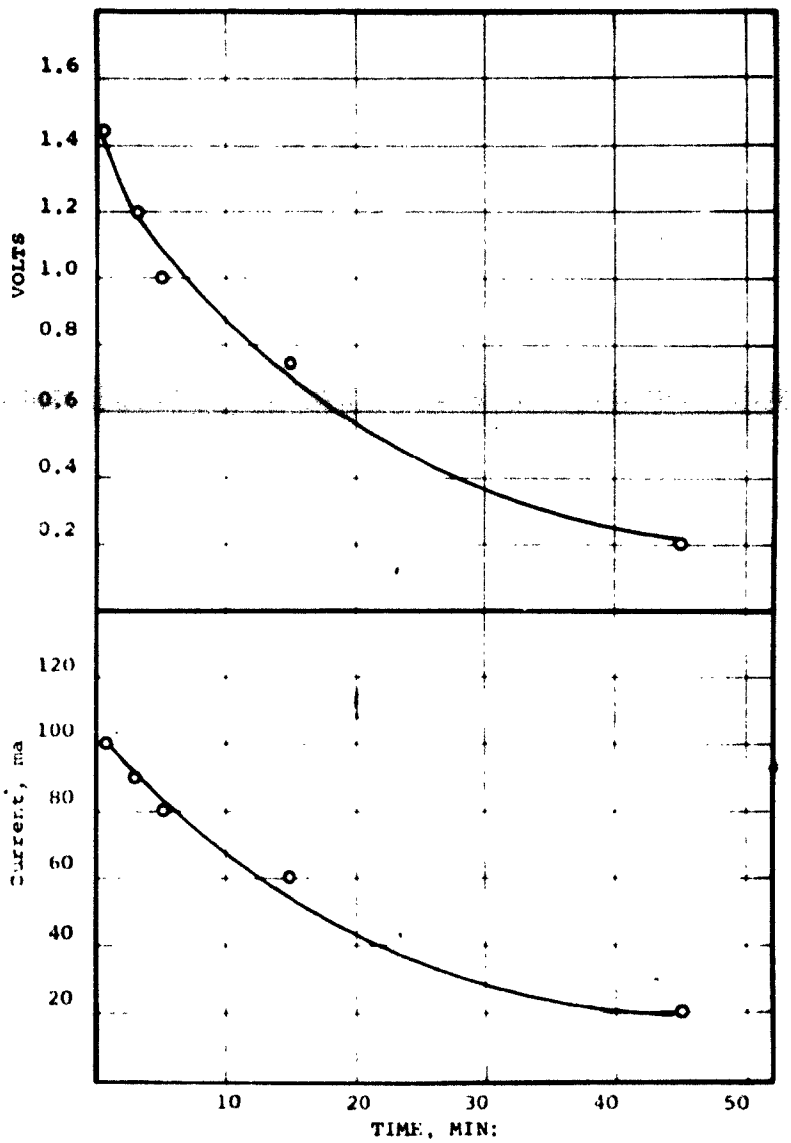
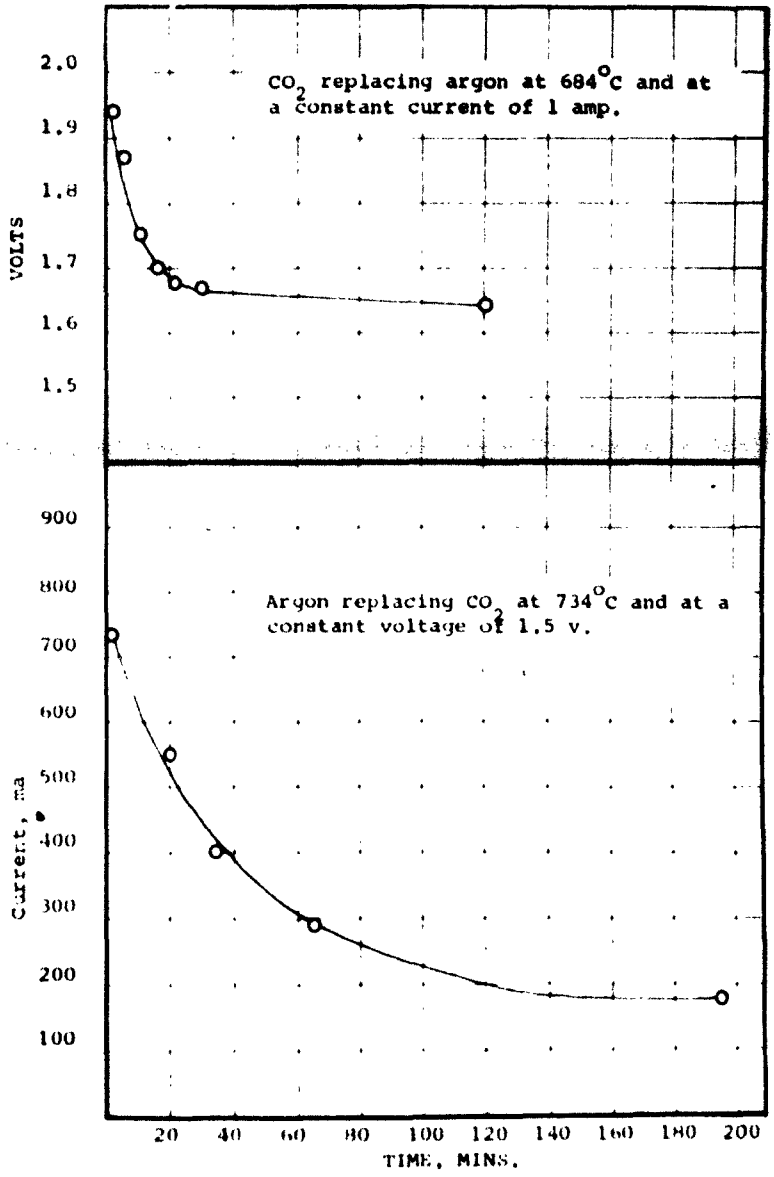


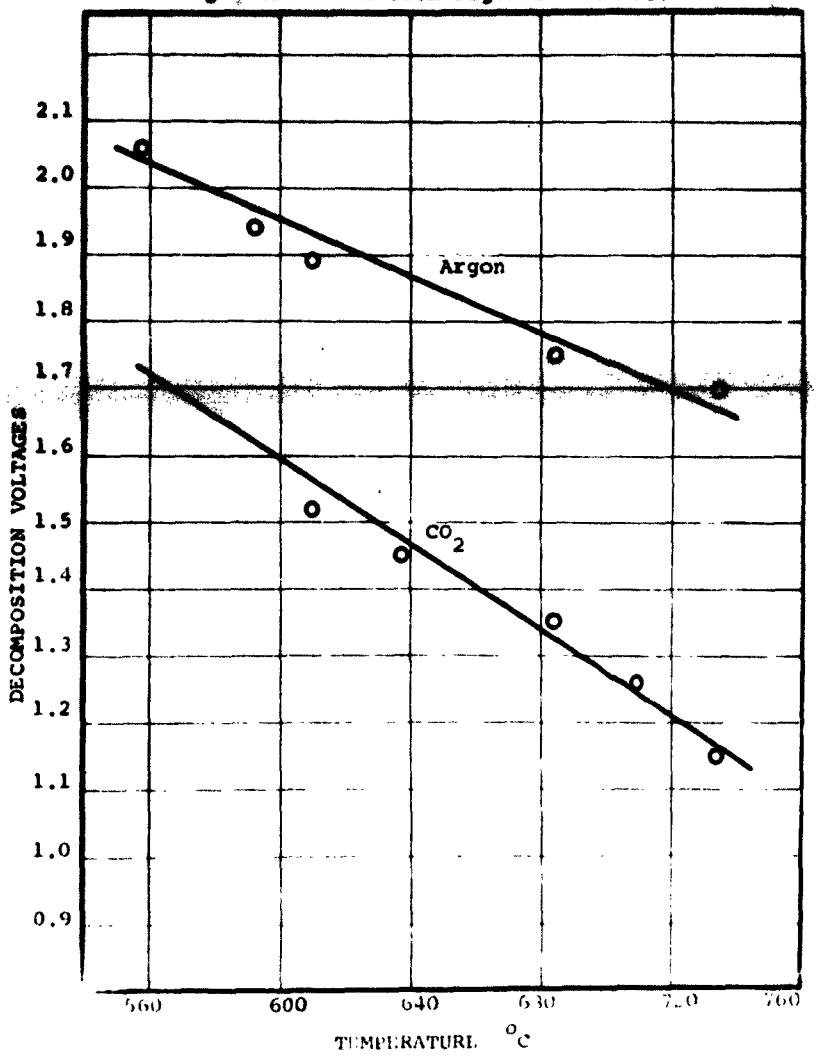
FIGURE 16. Current-time and voltage-time curves during replacement of one gas with the other.



the time that argon replaced carbon dioxide at 734°C, the current gradually decreased from 720 ma to 180 ma in about 200 minutes. In the other experiment, the current was maintained at 1 amp. while carbon dioxide was replacing argon. The voltage required for a current of 1 amp. at 684°C decreased, slowly from 1.95 to 1.65 volts in 120 minutes. These results are what would be expected from the current-voltage curves (Figures 6 - 11). They also show that carbon dioxide and not the metal electrodes are involved in the electrode reactions. The half-time for reaching a steady state voltage as CO_2 replaces argon at 684°C was about 8 minutes.

The change in decomposition voltages with temperature are plotted in Figure 17. With argon flowing through the cell, these voltages decrease from 2.06 at 558°C to 1.71 at 734°C. On the basis of the conclusions from the current-voltage curves, these values represent the voltages required for liberation of alkali element. It is not known yet whether this is lithium or sodium. At 558°C, there appears to be a second break in the current-voltage curve (Figure 13) at about 2.35 volts compared to about 2.06 volts for the first decomposition voltage. This difference may represent the difference in decomposition voltages for the deposition of lithium and sodium at this temperature. Comparison of the curves for argon and carbon dioxide indicates a difference of about 0.4 volt for the direct reduction of carbon dioxide and the liberation of alkali metal. The values for the decomposition voltages with carbon dioxide apply only to the particular cathode used in these experiments. The magnitude of the overvoltage or polarization effects arising from the kinetics of the gas-solid-liquid reaction at the cathode are not yet known. Any given electrode may also change with time in this respect owing to deposition of carbon or inactivation. In order to derive thermodynamic values from such measurements, it would be necessary to set up a system with references electrodes in a cell designed for the purpose. However, the results of the experiments reported here are valuable for the design of a practical electrolysis cell.

FIGURE 17. Effect of Temperature on Decomposition Voltages Estimated from Figures 12 and 13.



The electrolysis cell was operated continuously for over two weeks at temperatures from 550°C to 734°C. When measurements were not in progress, from 0.5 to 1.0 amps was passing through the cell. Carbon dioxide was passed through the cathode most of the time and argon the remainder of the time. The cell was operating satisfactorily when it was stopped to use the furnace for other experiments.

Examination of the cell after it was dismantled showed some corrosion of the stainless steel beaker, particularly at the surface of the liquid carbonate on the anode side where oxygen was liberated. The thin wire screen diaphragm was also partially oxidized and corroded. Neither the platinum anode nor the steel cathode were significantly affected. Apparently, the spiral passages through the wires of the steel brush were still open and the carbon that was formed was apparently transferred to the liquid melt. Considerable carbon was suspended in the liquid but most of it had settled to the bottom. The particle size of the carbon was such that it could be readily filtered.

Although the corrosion was not extensive, it was apparent that long periods of operation at temperatures above 700°C would require careful choice of materials of construction.

Reaction of Alkali Metals with Fused Carbonates:

Readings of the temperature and pressure were taken at intervals of from 5 to 10 minutes for the following runs:

a. Reaction of carbon dioxide with sodium
b. Reaction of carbon dioxide with sodium in the presence of fused alkali carbonates
c. Reaction of excess carbon dioxide with sodium in the presence of fused alkali carbonates
d. Reaction of carbon dioxide with lithium
e. Reaction of carbon dioxide with lithium in the presence of fused alkali carbonates
f. Reaction of carbon dioxide with potassium in the presence of fused alkali carbonates

The data for these runs are plotted in Figures 18 through 29. Three curves were obtained for each run: temperature vs. time, pressure vs. time, and pressure vs. temperature. The temperature vs. time curves show the rate of increase in temperature for each experiment. Changes in the rate of heating resulted when a new setting of the variable transformer was made. In some of the runs, the rapid reaction of carbon dioxide with the alkali metal caused a small increase in temperature as can be seen in Figures 24, 26, and 28 for lithium and potassium. This did not occur for the reactions involving sodium.

The pressure vs. time curves show the time at which the reactions started and also give an indication of the relative rates of the reactions. They also show which reactions did not proceed to completion. The temperature at which the reactions started and proceeded at a reasonable rate are more clearly shown in the pressure vs. temperature curves. When the reaction starts, the curve deviates from the straight line. For those reactions which accelerate rapidly with temperature, the curves fall abruptly.

The first experiment on the reaction of carbon dioxide with sodium (Figures 18 and 19) showed that the reaction was slow and did not take place rapidly at temperatures below 650°C. That a slow reaction was occurring above 450°C is shown in Figure 18. It was concluded that a coating of sodium carbonate or carbon prevented the rapid reaction.

In order to test the influence of surface coatings and to simulate the conditions that might exist in the electrolysis cell, an equal mole mixture of fused lithium carbonate, sodium carbonate, and potassium carbonate was added to the boat with the sodium. The curves in Figure 20 and 21 show that the reaction occurred more readily. A reasonably rapid reaction started at 575°C and accelerated with increase in temperature to 725°C where the reaction was reasonably complete. Thus, the presence of the fused carbonate mixture appreciably increased the ease of reaction of carbon dioxide with sodium. However, the reaction is still relatively slow as shown by the slow decrease in pressure with time in Figure 20. Similar results were obtained in Figure 22 and 23 in which the reaction was run in the presence of excess carbon dioxide.

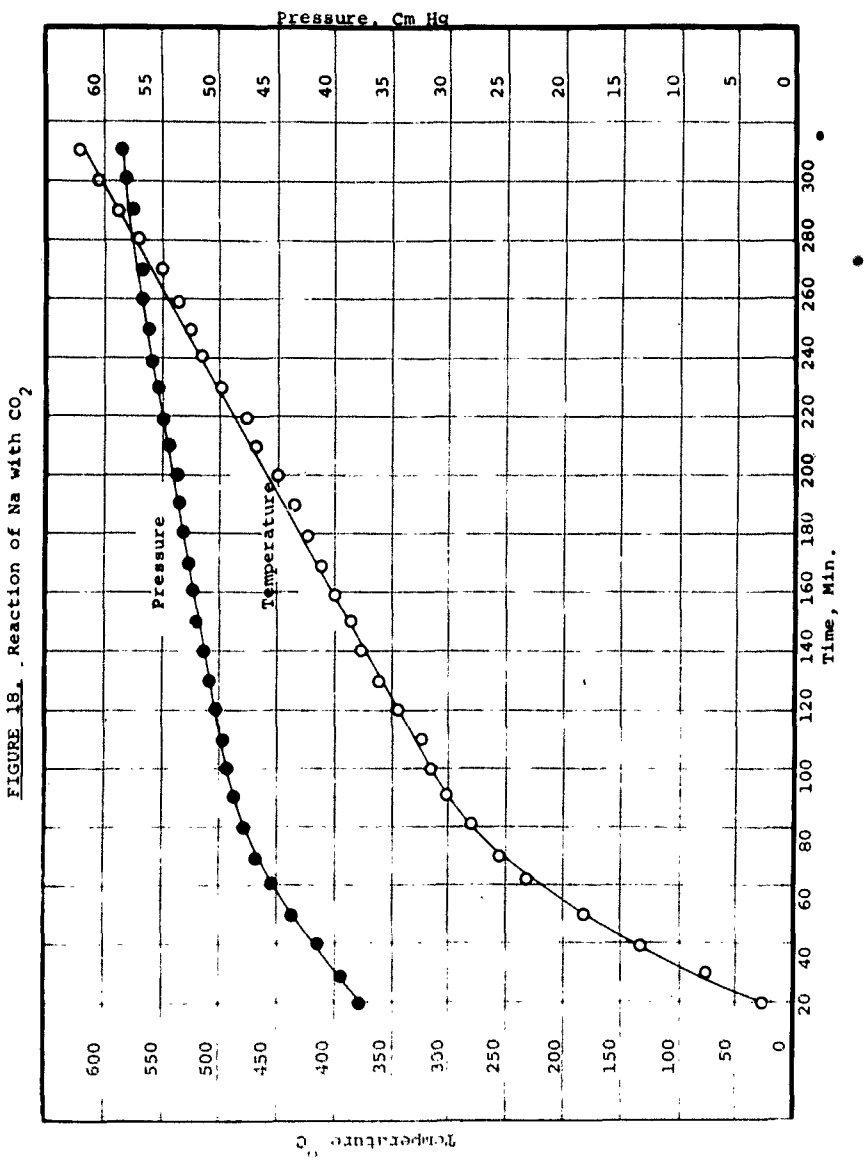
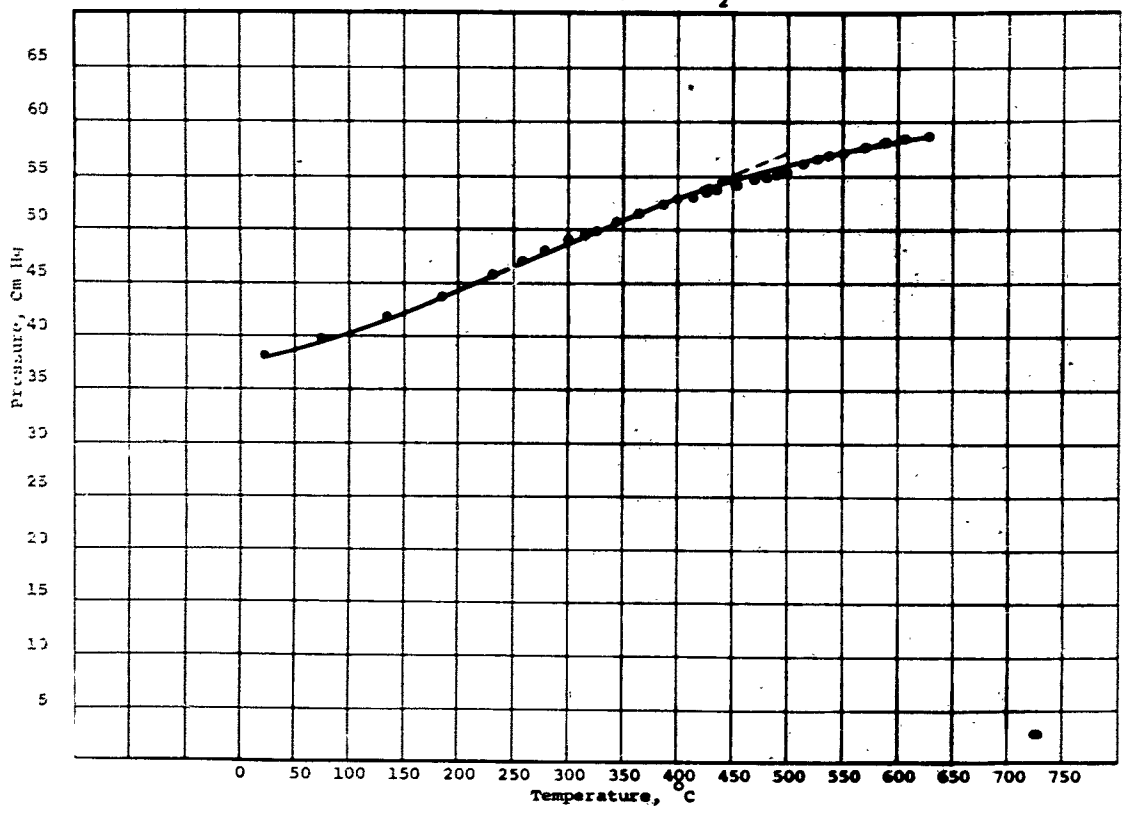


FIGURE 18. Reaction of Na with CO_2

FIGURE 19. Reaction of Mn with CO_2



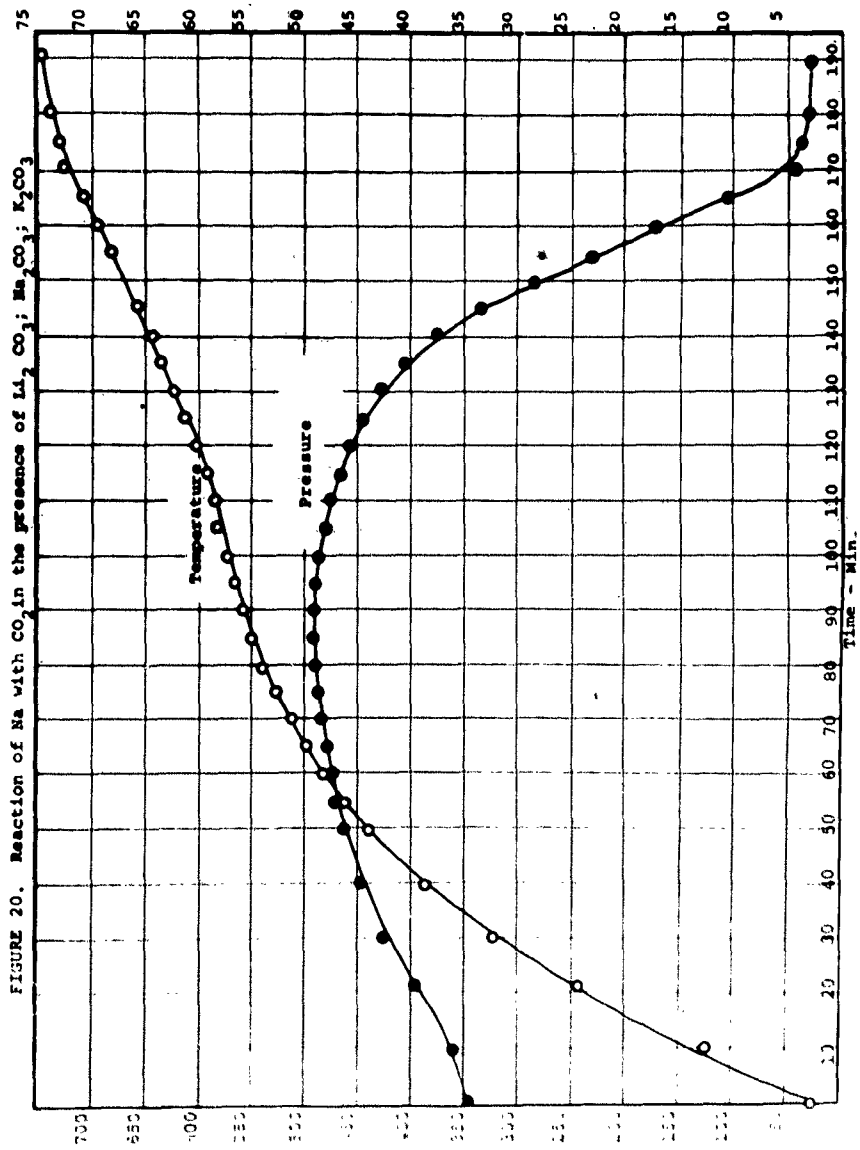


FIGURE 20. Reaction of Na with CO_2 in the presence of Li_2CO_3; Na_2CO_3; K_2CO_3

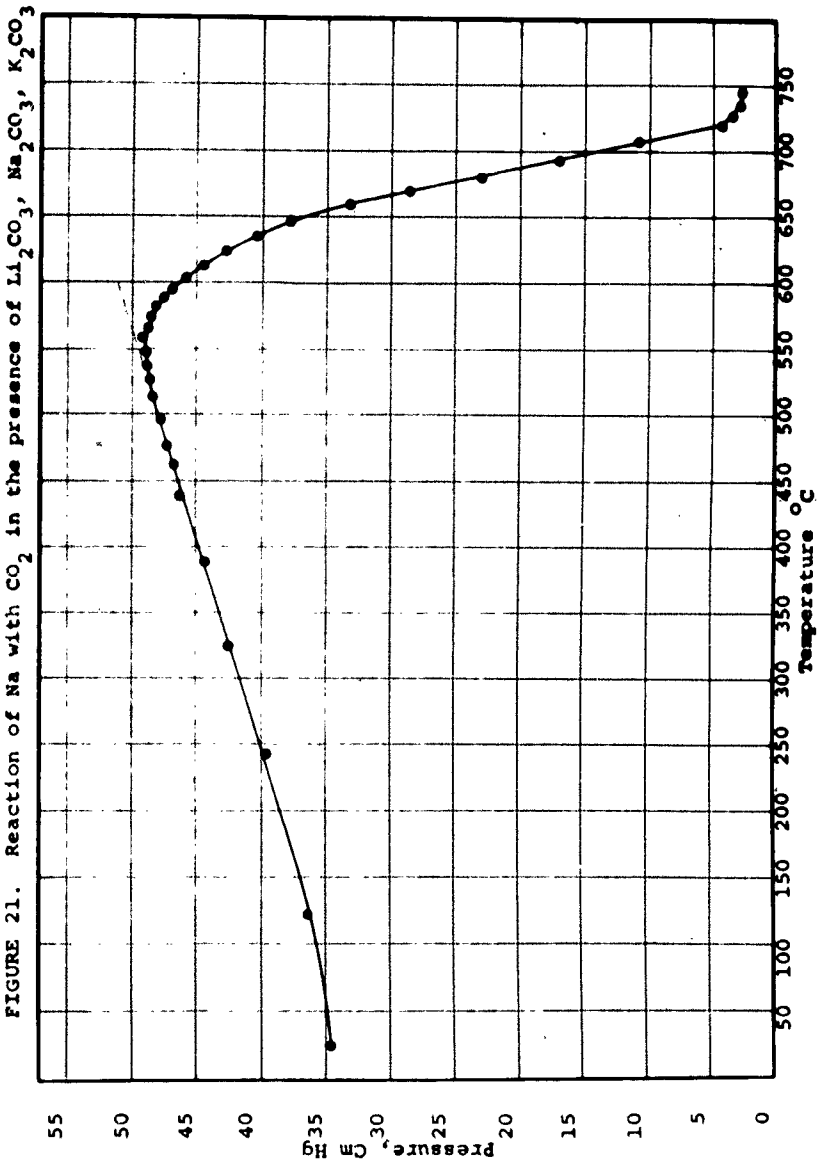


FIGURE 21. Reaction of Na with CO_2 in the presence of Li_2CO_3, Na_2CO_3, K_2CO_3

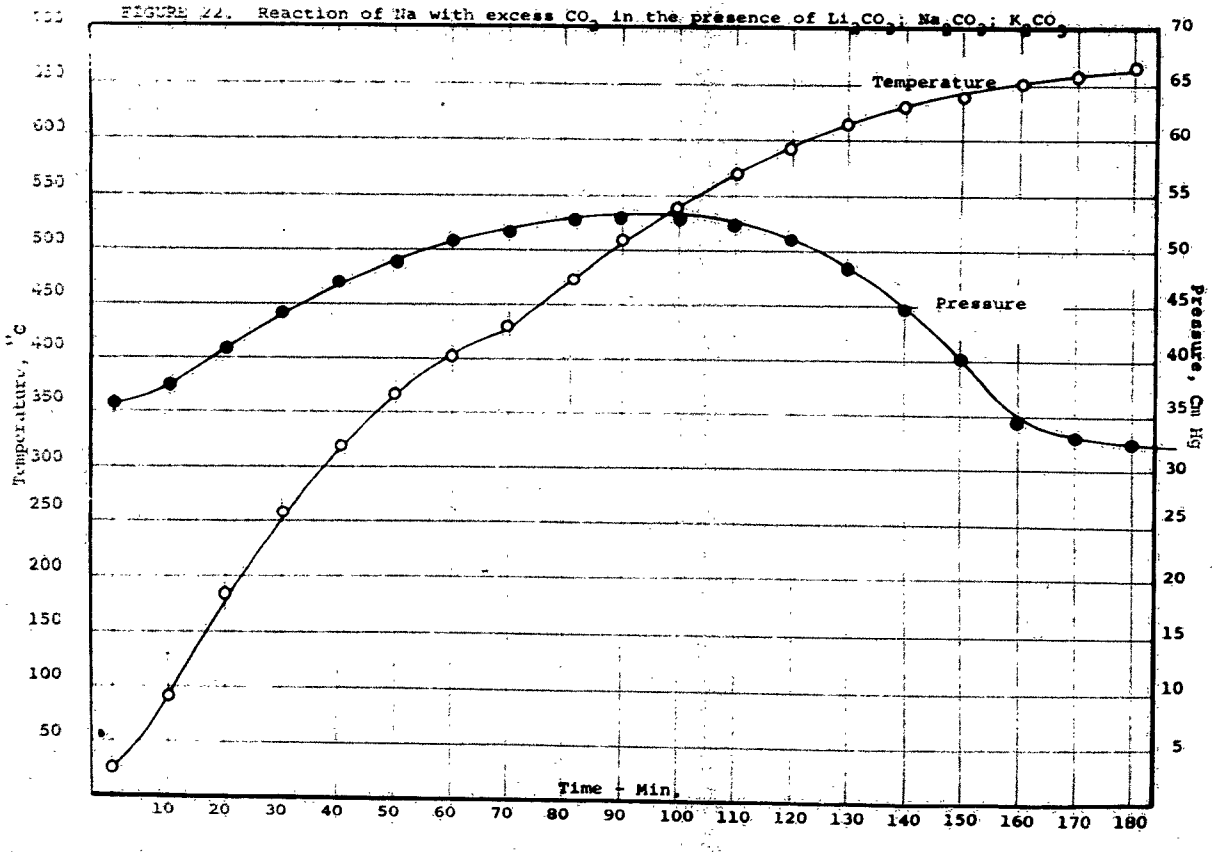


FIGURE 22. Reaction of Na with excess CO_2 in the presence of Li_2CO_3; Na_2CO_3; K_2CO_3

FIGURE 23. Reaction of Na with excess CO_2 in the presence of Li_2CO_3; Na_2CO_3; K_2CO_3

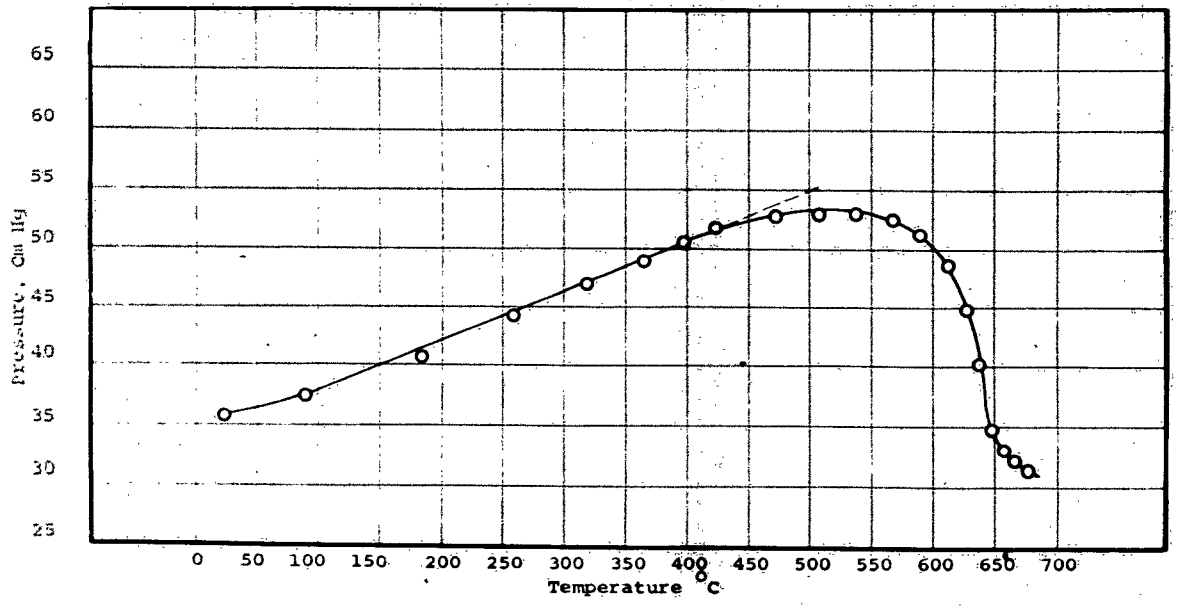
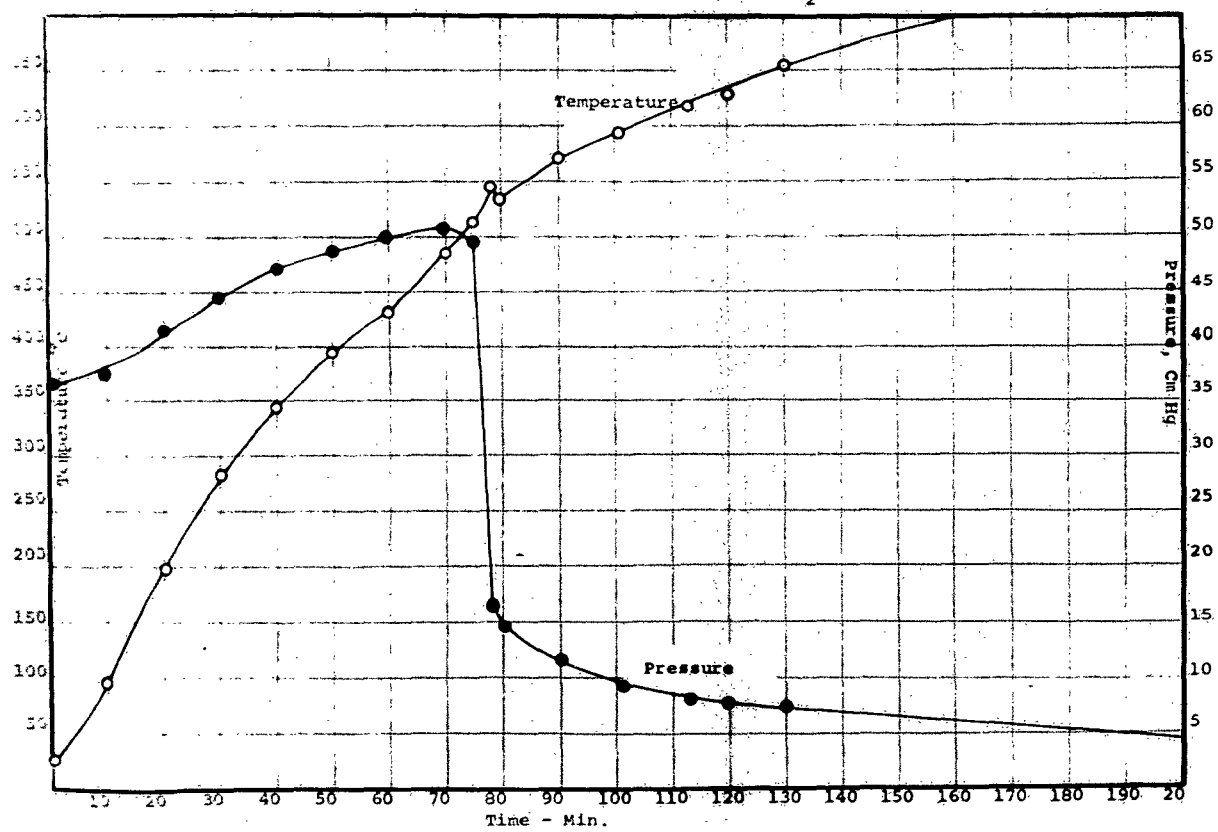


FIGURE 24. Reaction of Li with CO_2



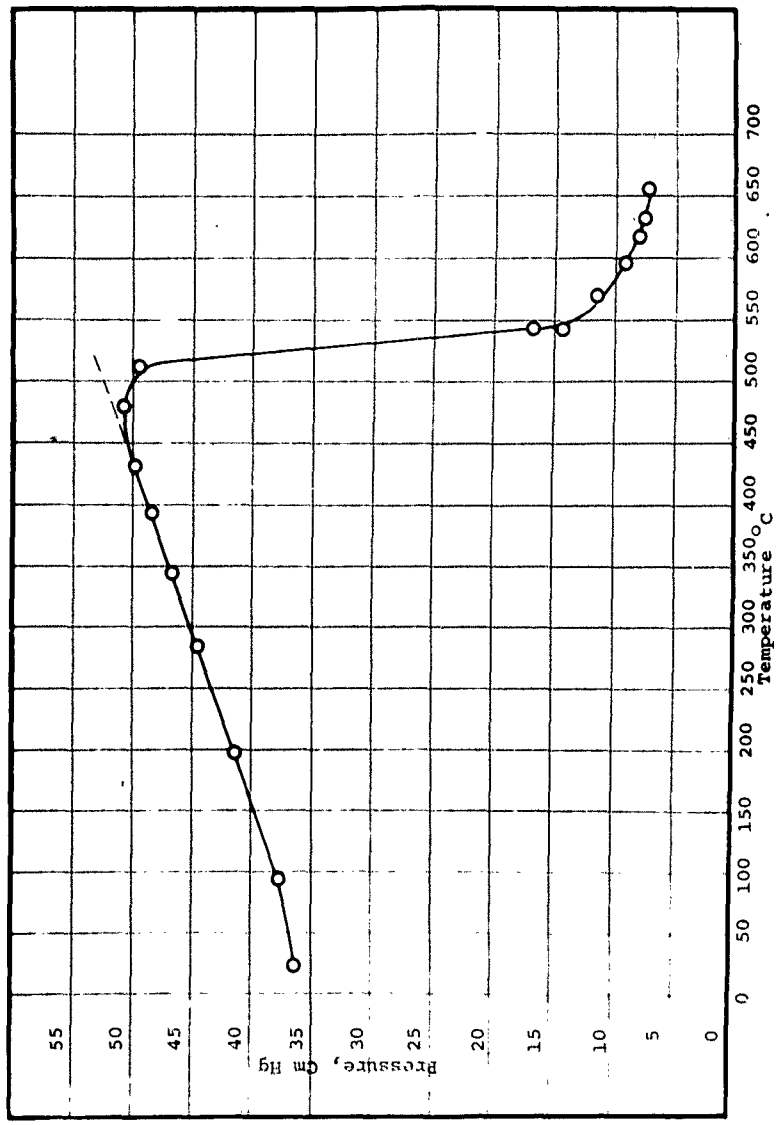
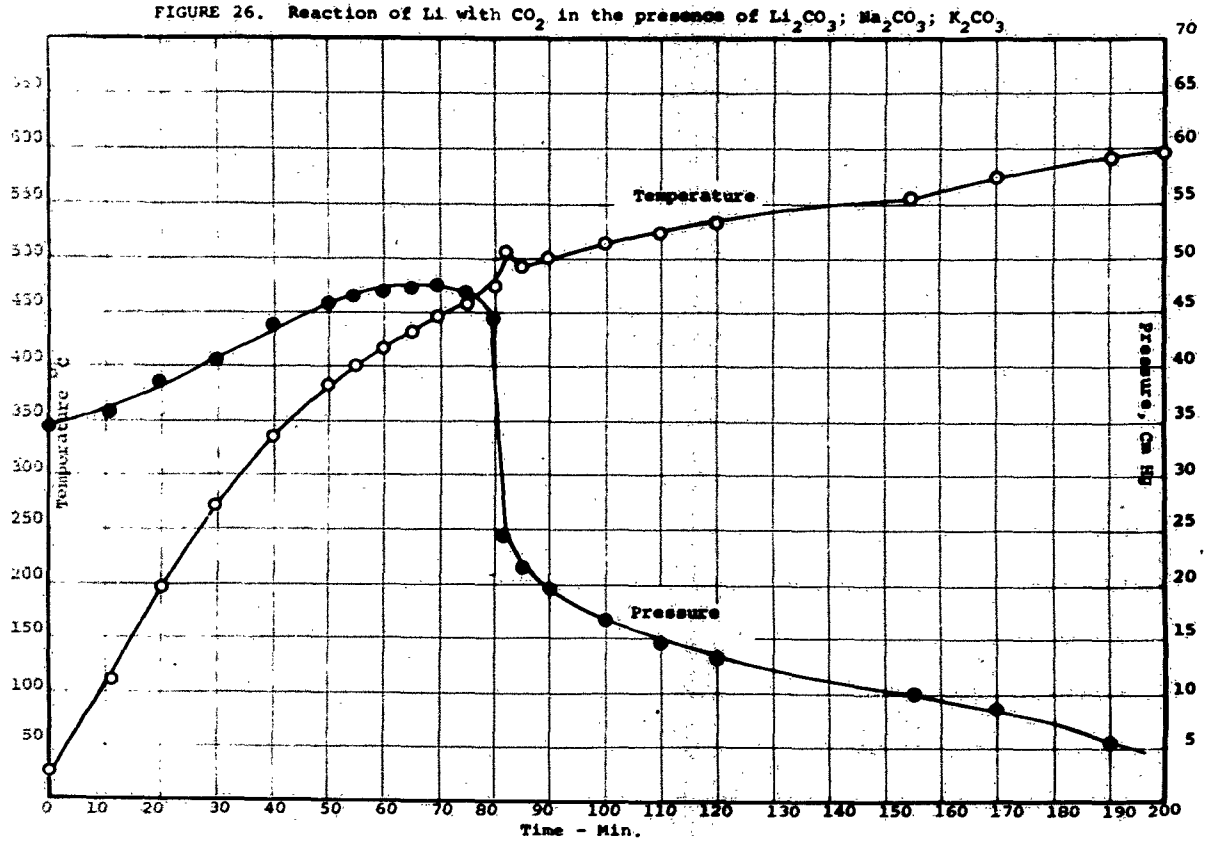


FIGURE 25. Reaction of Li with CO_2

FIGURE 26. Reaction of Li with CO_2 in the presence of Li_2CO_3; Na_2CO_3; K_2CO_3



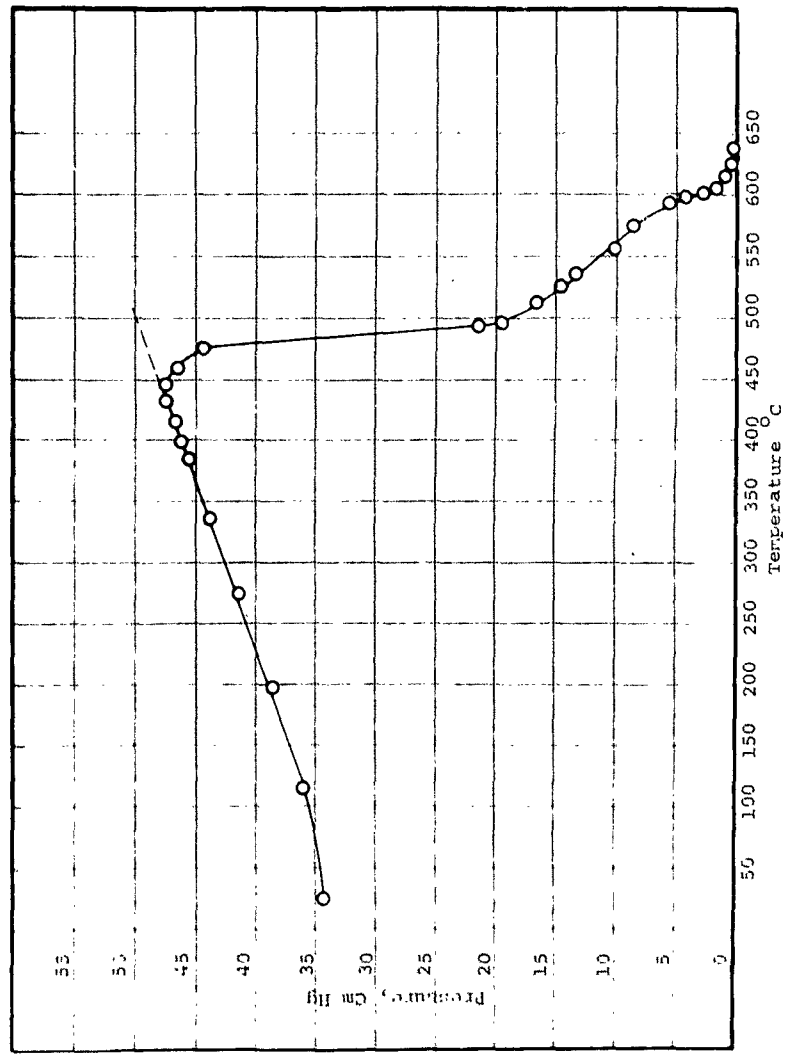
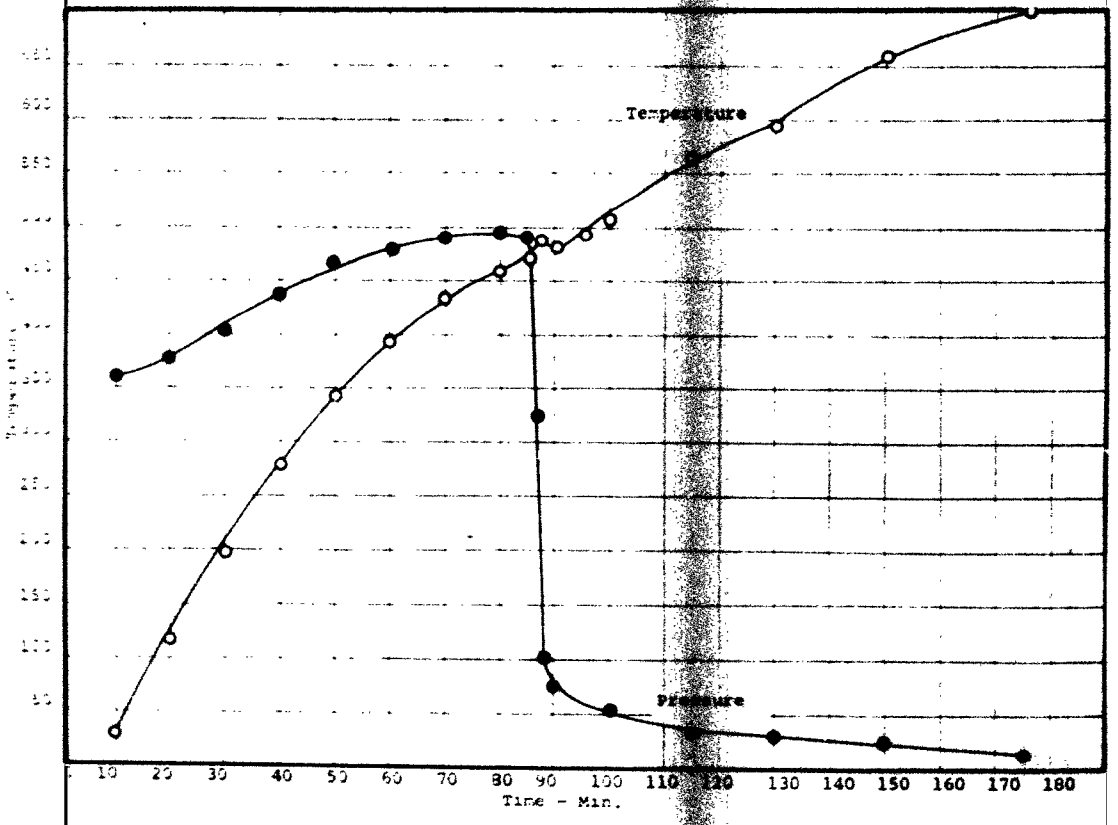


FIGURE 27. Reaction of Li with CO_2 in the presence of Li_2CO_3; Na_2CO_3;K_2CO_3

FIGURE 28. Reaction of K with CO_2 in the presence of Li_2CO_3; Na_2CO_3; K_2CO_3



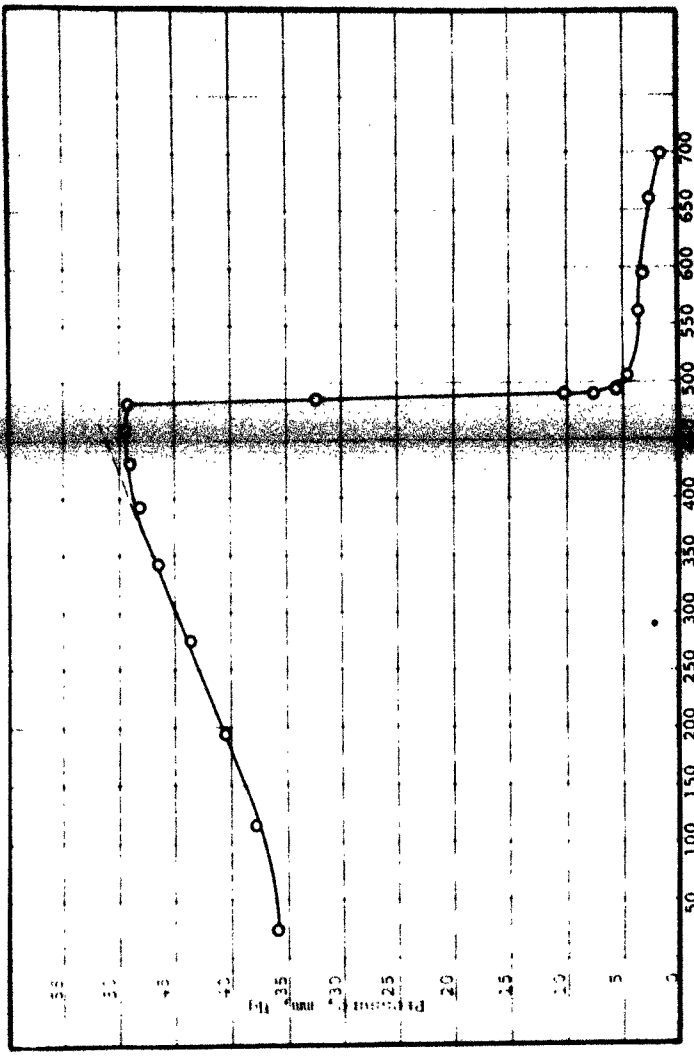


FIGURE 29. Reaction of K with CO_2 in the presence of Li_2CO_3; Na_2CO_3; K_2CO_3

The results shown in Figures 24 and 25 for the reaction of carbon dioxide with lithium show that the reaction occurs rapidly at a significantly lower temperature. Thus, at 500°C - 525°C, the reaction is very rapid. The pressure vs. time curve in Figure 24 indicates that the reaction became slower towards the end of the reaction. This may be due to the formation of a coating on the lithium or to the formation of carbon monoxide.

When the reaction was carried out in the presence of the fused carbonate, the reaction occurred at lower temperature, 450 - 500°C. There is still an indication of two stages to the reaction as indicated in Figures 26 and 27.

The results of the reaction of carbon dioxide with potassium (Figures 28 and 29) show that the reaction occurs rapidly at about the same temperature as that with lithium, 450 - 500°C. Instead of slowing down as with lithium, the reaction continues until it is nearly completed. In this respect, the reactions of lithium and potassium are different, but they are similar in that they react at an appreciably lower temperature than sodium does.

SOLID OXIDE ELECTROLYTES

Results of the conductivity measurements are shown in Figures 3, 4, and 5. As can be seen from the curves, the conductivity increases with temperature. This indicates an activated conduction process and, indeed, a plot of the logarithm of the current versus the reciprocal of the absolute temperature with voltage as the parameter yields a series of straight lines all having the same slope. It is seen that at the high temperatures appreciable current flows. As an example of the ability of a cell utilizing this material as an electrolyte to decompose carbon dioxide, consider the operation of the cell at 750°C with 30 volts imposed across the electrodes. The current flowing is 0.36 amps.

The following calculation is made:

$$0.36 \text{ amps} = \frac{0.36 \text{ coulombs}}{\text{Sec.}} \times \frac{3600 \text{ sec.}}{\text{Hr.}} = 1300 \text{ coulombs/hr.}$$

96,500 coulombs = 1 equivalent weight

Equivalent weight of O = 8 grams

$$\text{So } \frac{1300}{96{,}500} \times 8 \times \frac{44}{32} = 0.148 \text{ grams } CO_2 \text{ decomposed/hr.}$$

These results are for a cell having a disc 3.8 mm thick and 2.0 cm^2 in area. If it is assumed that the resistance of the electrolyte is proportional to the thickness and inversely proportional to the area, then it can be shown that reduction of the thickness of the electrolyte disc to 0.025 mm and increasing the area of the disc to 4 cm^2 would enable the cell to decompose approximately 1 gram mole of carbon dioxide per hour, the average amount expired by a human. Such a reduction in thickness is well within the range of modern plasma spraying and vacuum deposition techniques and should lead to construction of compact, efficient solid electrolyte cells.

The analysis of the gas from the positive electrode compartment for a run in which CO_2 was fed to the negative electrode compartment indicates the presence of oxygen in far higher concentration than it appears in air. It should be remembered that this cell was not gas-tight.

For the gas-tight cell using the zirconia-yttria electrolyte tube, both the gas chromatographic results and the pressure increase on the air side of the cell show the production of oxygen by the cell. The presence of carbon monoxide in the other side of the cell indicates the decomposition of the carbon dioxide in the cell. Several estimates of various operating efficiencies can be made. The current of 300 milliamps flowed for three hours. If the conductivity of the solid electrolyte were purely ionic, then about 200 cc of oxygen would have been produced. Actually, only about 15 cc of oxygen were produced, indicating that the conductivity of the solid electrolyte was only about 7.5% ionic with the remainder being electronic.

The active area of the cell was about 15 cm^2 so that the production of 15 cc of oxygen in three hours indicates a production rate of about 0.3 $cc/cm^2/hr$.

The detection of oxygen and carbon monoxide proves unequivocally the operation of the cell in the predicted fashion. The low efficiency of the present device is easily explained. The material used in the fabrication of the solid electrolyte tube was commercial zirconia and yttria of average purity but not the high purity required for a device of this kind because the tube was not fabricated with this application in mind. Use of impure oxides is known to cause electronic conduction in oxides which when pure conduct wholly ionically. It has previously been demonstrated at Isomet that use of pure oxides results in a product that conducts purely ionically. In addition, these tubes were fired at temperatures in the region of 2000°C under what could well have been slightly reducing conditions. Under these conditions, it is known that the resulting product could have appreciable electronic conductivity. Since these tubes are the only ones available on even a custom basis, this points up the need to develop fabrication techniques for the highly pure oxides required in the solid electrolyte.

CONCLUSIONS

MOLTEN CARBONATE ELECTROLYTES

The experiments described here indicate that it is possible to operate the electrolysis cell in two ways; carbon dioxide can be reduced directly or alkali metal can be deposited and carbon dioxide reduced indirectly by reaction with the alkali metal. Direct reduction of the carbon dioxide at current densities of the order of 0.1 amp/cm^2 (ca. 100 amp/ft^2) would require temperatures of 700°C or higher. This might be increased appreciably with more active cathode arrangements. Because of the probability of corrosion at high temperatures and because of the limitation on current density, the direct reduction of carbon dioxide will require more experimental work for design of a practical cell. The operation at high temperature, however, does have the possibility of obtaining carbon monoxide rather than carbon as the principal product in the cell. In this case, the carbon monoxide would be decomposed to carbon and carbon dioxide external to the cell.

In view of the above considerations, the formation of alkali metal and its reaction with carbon dioxide should receive further experimental consideration. The electrolysis can be carried out at lower temperatures and at higher current densities. However, the cell design will be somewhat different from one for the direct reduction of carbon dioxide. Special consideration must be given to the efficient contacting of the carbon dioxide with the liberated alkali metal. The lower temperature of operation will undoubtedly result in more carbon formation within the cell. In fact, it may be desirable to promote this reaction within the cell rather than decompose carbon monoxide external to the cell. In this case, pumping and filtering or centrifuging will be required, but as explained in an earlier section, this may be necessary anyway for zero gravity operation.

Reaction of Alkali Metals with Fused Carbonates:

The results of the experiments reported here show clearly that lithium and potassium react with carbon dioxide much more readily than sodium does. Temperatures as high as 700°C may be required for the reaction with sodium as compared to 550°C for lithium or potassium. It is desirable, therefore, that lithium or potassium be electrodeposited rather than sodium.

Unfortunately, decomposition voltages for the electrolysis of the fused alkali carbonates are not available. Calculated values for the alkali chlorides (W. J. Homer, M.S. Malmberg and B. Rubin, J. Electrochem. Soc. 103, 8 (1956) at 600°C are as follows: Na^+ 3.42, Li^+ 3.57, K^+ 3.66, Rb^+ 3.59, Cs^+ 3.60. If it is assumed that the decomposition voltages for the alkali carbonates are in the same order, it is seen that sodium would be preferentially deposited from an equal mole mixture of the lithium, sodium and potassium carbonates. Consequently, it is concluded that the electrolyte should be a mixture of lithium and potassium carbonates rather than a mixture of the three carbonates.

Melting point data show that the mixtures of lithium and potassium carbonates are satisfactory. They are as follows: Li_2CO_3 726°C, K_2CO_3 899°C, (Li_2CO_3.K_2CO_3) 504.5°C, (0.427 Li_2CO_3 0.573 K_2CO_3) 498°C, (0.62 Li_2CO_3 0.38 K_2CO_3) 488°C. In accordance with these conclusions, a eutectic mixture of lithium and potassium carbonate has been prepared for use in an electrolysis cell. This cell is designed for reasonably efficient contacting of gaseous carbon dioxide with electro-deposited lithium and potassium.

SOLID OXIDE ELECTROLYTES

It can be seen that improvements in this operation can be made. Use of an electrolyte with 100% ionic conductivity, increasing the applied voltage to 10 volts, use of thorium-yttrium or thorium-lanthanum oxides which have higher ionic conductivity than the zirconium-yttrium oxide system, increasing the operating temperature and reducing the thickness of the solid electrolyte could result in a cell with greatly improved production rates.

In conclusion, the principle of operation of this device has been demonstrated beyond question. Based on the results obtained, it is concluded that a compact, efficient, solid-electrolyte cell can be constructed that will decompose carbon dioxide at any desired rate, the rate of decomposition being dependent on temperature, applied voltage, cell configuration and fabrication techniques. In view of the promise shown by this system, Isomet has applied for United States Patents covering the manufacture and use of this solid-electrolyte system.

RECOMMENDATIONS FOR FUTURE RESEARCH

It is recommended that development of the solid electrolyte system be continued because of the favorable results obtained to date and because of the inherent simplicity, freedom from gravitational effects and elegance of the process. Emphasis should be placed on development of fabrication techniques for producing solid electrolyte configurations having the desired physical, chemical, and electrical properties and on the integration of the cell into a complete oxygen recovery system. In particular, emphasis should be placed on use of modern ceramic fabricating techniques such as plasma jet spraying, slip casting and extrusion to develop usable forms of the solid electrolyte.

Aerospace Medical Division, 6570th Aerospace Medical Research Laboratories, Wright-Patterson AFB, Ohio Rpt. No. MRL-TDR-62-16. STUDY OF ELECTROLYTIC REDUCTION OF CARBON DIOXIDE. Final report, Mar 62, vi + 53p. incl. illus. Unclassified report

Electrolytic methods for regeneration of oxygen from carbon dioxide were studied to design a closed-cycle life support system. Two different electrolyte systems were studied: molten alkali carbonates and solid oxides. Mixtures of lithium and potassium carbonates were suitable and could be operated in two different fashions. If operated below the decomposition voltage of the alkali carbonates, the

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1. Closed Cycle Ecological Systems (Space Biophysics)
2. Electrolysis (Chemical Reactions)
3. Controlled Atmospheres (Physical and Physiochemical Concepts)

I. AFSC Project 6373, Task 637302
II. Life Support Systems Laboratory
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V. Chandler, H.W., Oser, W.
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